

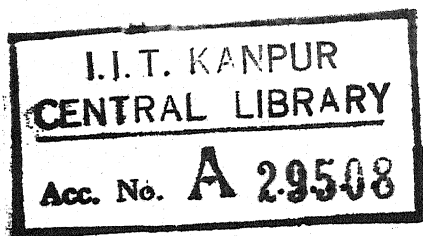
✓STUDIES IN VALENCE ISOMERISM IN HETEROSYSTEMS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
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to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
MARCH 1974



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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE I

This is to certify that Mr. K. B. Sukumaran has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 500 Mathematics for Chemists
Chm 501 Advanced Organic Chemistry I
Chm 502 Advanced Organic Chemistry II
Chm 521 Chemical Binding
Chm 523 Chemical Thermodynamics
Chm 524 Modern Physical Methods in Chemistry
Chm 541 Advanced Inorganic Chemistry I
Chm 611 Fascinating Problems in Organic Chemistry
Chm 611 Theory of Electrocyclic Reactions and Cycloadditions
Chm 662 Chemical Kinetics
Chm 800 General Seminar
Chm 801 Special Graduate Seminars
Chm 900 Graduate Research

Mr K. B. Sukumaran successfully completed his Ph.D. Qualifying Examination in August 1970.

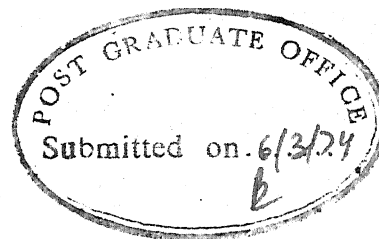
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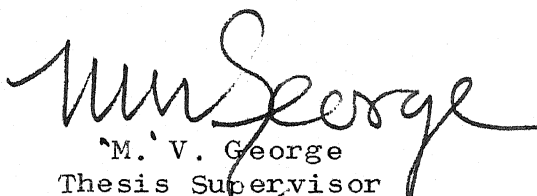
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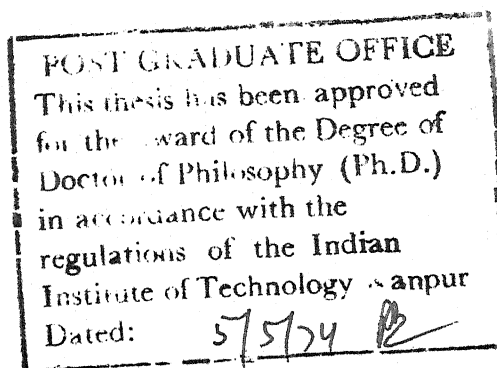
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CERTIFICATE II

Certified that the work contained in this thesis entitled: "Studies in Valence Isomerism of Heterosystems", has been carried out by Mr. K. B. Sukumaran under my supervision and the same has not been submitted elsewhere for a degree.


M. V. George
Thesis Supervisor



ACKNOWLEDGEMENTS

It is my pleasure to place here on record my deep sense of indebtedness and gratitude to Professor M. V. George for the kind encouragement, guidance and supervision that I received from him throughout my tenure as a graduate student here.

My sincere appreciation and thanks are also due to Professors C. N. R. Rao, P. T. Narasimhan, D. Devaprabhakara and S. Ranganathan and all the other members of the Chemistry faculty for the unreserved help I received from them and for their keen interest in my progress.

Of a number of my colleagues in the department who have been of invaluable help to me, I would like to make special mention of Dr. C. S. Angadiyavar, Dr. K. S. Balachandran, Mr. R. K. Gupta, Mr. R. Balasubramanian, Miss S. Lahiri, Dr. M. S. Gopinathan and Mr. S. Aravamudhan. I am also thankful to my other innumerable friends both in the department and in the hostels who have contributed immensely to make my stay in Kanpur a pleasant and memorable one.

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Assistance received from Mr. A. H. Siddiqui, in the microanalyses of samples, from Mr. J. N. Sharma and others of the Glass Workshop, Mr. K. K. Bajpai, Mr. R. D. Singh and others of the Chemistry departmental office, and the staff of the Graphic Arts is gratefully acknowledged.

I wish to thank Mr. Nihal Ahmad for the typing of this thesis, Mr. J. N. Tripathi for drawing the schemes and figures, and Mr. Banarasi Lal for the all-round help I received from him.

Financial assistance in the form of Research fellowships from the Council of Scientific and Industrial Research during the earlier half and Research Assistantship from the authorities of the Indian Institute of Technology, Kanpur during the latter half of my graduate work, is acknowledged with gratitude.

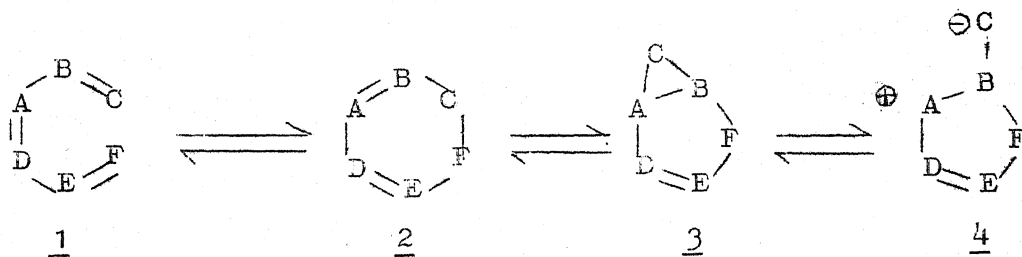
Whatever I am today and whatever I hope to be in future, have all been made possible only because of the affectionate encouragement and unreserved help in abundance I received from my uncles, Mr. G. K. Menon and Mr. K. A. Menon. The sacrifices made by my parents to ensure my education both in the undergraduate and graduate levels are also acknowledged with a sense of everindebtedness and gratitude.

K. B. Sukumaran

PREFACE

Studies of valence isomerisations have received considerable attention in recent years, especially since the formulation of ^{the} principles of conservation of orbital symmetry. In the thesis entitled: "Studies in Valence Isomerism of Heterosystems", we have attempted a detailed investigation of some aspects of the chemistry of 1,2-bisphenylazoalkenes, wherein their valence isomeric forms are involved.

Chapter 1 contains a general survey of the literature dealing with the valence isomerisations of hetero-1,3,5-hexatrienoids. A heterotrienoid system like (1) can exist in different valence isomeric forms (2)-(4) as shown below and several reactions of these systems can be rationalised in terms of this behaviour. In this Chapter, we have cited specific



examples of several reactions which are reported in the literature and which come under this category.

In Chapter 2, we have discussed the results of our studies on the thermal and photochemical fragmentations of

1,2-bisphenylazoalkenes formed in the nickel peroxide oxidation of 1,2-diketone bisphenylhydrazones. It has been possible to show that the thermolysis of 1,2-bisphenylazostilbene yields 2,4,5-triphenyl-1,2,3-triazole. The same triazole was obtained when a benzene solution of 1,2-bisphenylazostilbene was subjected to photolysis. Similarly, the corresponding 2-phenyl-4,5-diaryl-1,2,3-triazoles were obtained both in the thermolysis and photolysis of 1,2-bisphenylazodi(4-chlorophenyl)ethylene and 1,2-bisphenylazodi(4-methoxyphenyl)ethylene. The thermolysis of 1,2-bisphenylazocyclohexene gave rise to the expected 2-phenyl-4,5-tetramethylene-1,2,3-triazole. On the other hand, photolysis of 1,2-bisphenylazocyclohexene gave a mixture of products consisting of 2-phenyl-4,5-tetramethylene-1,2,3-triazole and 1-anilino-2-phenyl-1,4,5,6-tetrahydrocyclohexa[d]-1,2,3-triazole. The thermolysis and photolysis of both 1,2-bisphenylazoethylene and 2,3-bisphenylazo-2-butene, however, failed to give the expected triazoles. But 2,3-bisphenylazo-2-butene when irradiated in presence of dry HCl gas gave 2-phenyl-4,5-dimethyl-1,2,3-triazole. The formation of triazoles in these reactions has been explained in terms of an initial valence isomerisation of the starting bisphenylazoalkenes to the corresponding mesoionic anhydro 1-phenylimino-2-phenyl-4,5-disubstituted-1,2,3-triazolium hydroxides, which subsequently lose phenylnitrene to yield the corresponding triazoles. Our attempts to trap the phenylnitrene formed in these reactions, however, were not successful.

The photolysis of 1,2-bisphenylazoacenaphthylene in benzene solution failed to give rise to the expected 1,2-acenaphtho[d]-1,2,3-triazole. A similar observation was made when the reaction was carried out under conditions of thermolysis also. However, when the photolysis of 1,2-bisphenylazoacenaphthylene was carried out in a mixture of methanol and methylene chloride, 1,2-acenaphthenequinone monophenylhydrazone was formed as the only isolable product. In continuation with our studies, we have examined the thermal and photochemical behaviour of o-(phenylazo)phenyldiazocyanide and an azomethine imine like C-biphenylene-N ^{α} -(4-chlorophenyl)-N ^{β} -cyanoazomethineimine. Photolysis and thermolysis of o-(phenylazo)phenyldiazocyanide gave the expected 2-phenylbenzotriazole. The thermolysis of C-biphenylene-N ^{α} -(4-chlorophenyl)-N ^{β} -cyanoazomethineimine gave 9-fluorenone-N-(4-chlorophenyl) anil, as the only isolable product. Photolysis of the same azomethineimine on the other hand, gave a mixture of 9-fluorenone and 9-fluorenone-N-(4-chlorophenyl) anil.

In Chapter 3, we have advanced some chemical evidences for the iminotriazolium intermediates formed from bisphenylazoalkenes. It was pointed out earlier that a bisphenylazoalkene such as 1,2-bisphenylazostilbene can exist in its valence isomeric form, namely, anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide. We have shown that the iminotriazolium intermediate behaves like a 1,3-dipolar system (azomethineimine) and that it undergoes cycloadditions with several acetylenic

and olefinic dipolarophiles. Thus, the reaction of 1,2-bisphenyl-azostilbene with dimethyl acetylenedicarboxylate gave rise to a pyrazoline- $[2,3-c]$ $[1,2,3]$ triazole derivative. Other acetylenic dipolarophiles that have been employed, include methyl propiolate and dibenzoylacetylene. Similar cycloadditions were observed in the cases of 1,2-bisphenylazodi(4-chlorophenyl)ethylene, 1,2-bisphenylazodi(4-methoxyphenyl)ethylene and 1,2-bisphenylazocyclohexene. The reaction of these bisphenylazoalkenes with different olefinic dipolarophiles like dimethyl maleate, dimethyl fumarate, ethyl acrylate, acrylonitrile and methyl methacrylate have been tried and in each case the corresponding 4,5-dihydropyrazolino- $[2,3-c]$ $[1,2,3]$ triazoles were formed. On the other hand, triazolino $[1,5-c]$ $[1,2,3]$ triazole-5-ones and the corresponding thiones were formed when these 1,2-bisphenylazoalkenes were reacted with phenyl isocyanate and phenyl isothiocyanate, respectively. Similar cycloadducts are formed in the reaction of 2,3-bisphenylazo-2-butene with acetylenic dipolarophiles under acid catalysed conditions. The formation of all these products have been explained in terms of the anhydro 1-phenylimino-2-phenyl-4,5-disubstituted-1,2,3-triazolium hydroxides to the various dipolarophiles. The stereospecificity and the regioselectivity of these additions have also been examined. The concerted nature of these addition reactions was established by kinetic studies and through evaluation of the activation energy and entropy of activation of some representative cases.

Additional chemical evidence concerning the structure of these adducts was obtained from thermolysis studies of the cycloadducts of 1,2-bisphenylazostilbene with dimethyl maleate and dimethylfumarate. In both these cases, the thermolysis resulted in the formation of 2,4,5-triphenyl-1,2,3-triazole, thereby establishing the presence of the triazole moiety in these adducts.

Further proof for the existence of mesoionic iminotriazolium species probably in dynamic equilibrium with the bisphenylazoalkenes, has been derived from the reaction of these compounds with carbon disulphide. Reaction of carbon disulphide with the starting bisphenylazoalkenes resulted in the formation of ^{the} corresponding 2-phenyl-4,5-disubstituted-1,2,3-triazole, phenyl isothiocyanate and elemental sulphur. The formation of these products has been explained in terms of an initial 1,3-dipolar cycloaddition of anhydro 1-phenylimino-2-phenyl-4,5-disubstituted-1,2,3-triazolium hydroxides to carbon disulphide, followed by fragmentation of these cycloadducts.

In Chapter 4 of the thesis, we have summarised our attempted studies on the synthesis of a few heterocyclic systems by routes involving valence isomerisations. Thus, it has been shown that N,N'-dibenzal-o-phenylenediamine rearranges under thermal condition to 1-benzyl-2-phenylbenzimidazole. The intermediate dipolar imidazolium ylide, however, could not be trapped through cycloaddition reactions with different dipolarophiles. Similarly, 2,3-dihydro-5,6-diphenylpyrazine and

2,3-dihydro-2,3,5,6-tetraphenylpyrazine, prepared from the reactions of the corresponding ethylenediamines with benzil, also rearranged thermally to the corresponding imidazole derivatives. The formation of these imidazole derivatives has been explained in terms of an initial electrocyclic ring opening of the dihydropyrazines to the corresponding enediimines, followed by valence isomerisation and subsequent rearrangement of the enediimines. Our attempts to trap these dipolar intermediates through cycloaddition reactions did not meet with success. The dianil formed in the reaction of o-phthalaldehyde and aniline rearranged to 2-phenyl-1-phenyliminoisoindoline, and this transformation has been rationalised in terms of valence isomeric intermediates.

CHAPTER 1

VALENCE ISOMERISM IN
HETEROTRIENOID SYSTEMS

1.1 INTRODUCTION

Valence isomerisation as a class of concerted processes has been receiving detailed and systematic attention in recent years. Elaboration of the principles of orbital symmetry by Woodward and Hoffmann¹ and their application by a number of workers have provided an added momentum to research in this field.

The valence isomerisations involving cyclic as well as open-chain isomers, can be broadly classified on the basis of

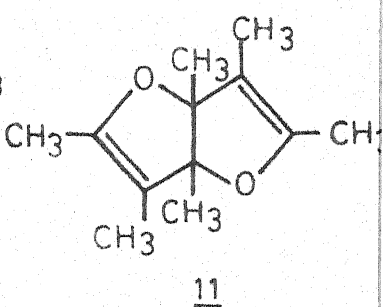
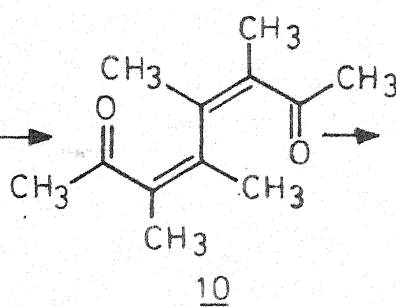
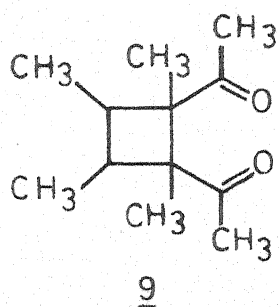
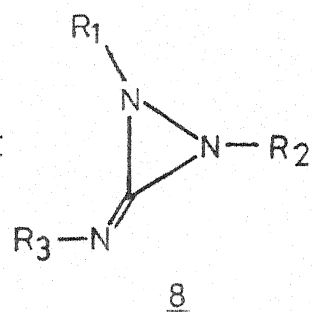
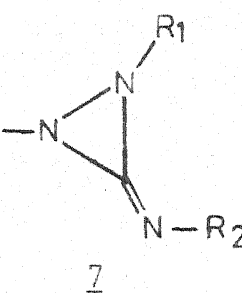
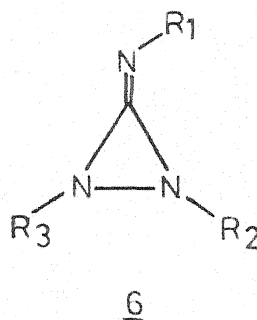
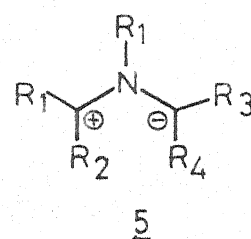
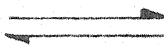
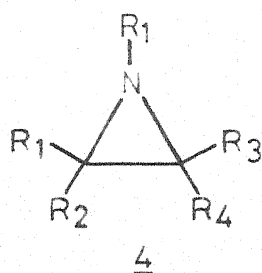
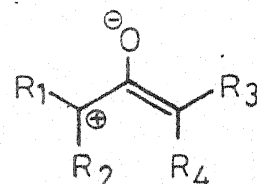
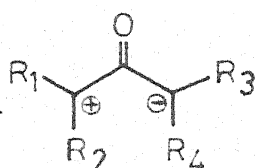
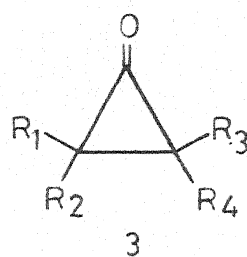
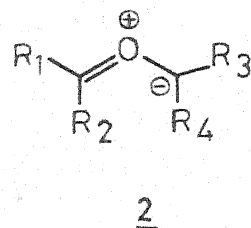
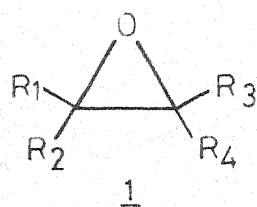
the ring size of the cyclic system. Some illustrative examples of valence isomerisation in few cyclic systems are listed in Scheme 1.1.

A typical instance of valence isomerism of three membered ring compounds is the thermal (conrotatory) and the photochemical (disrotatory) opening of an epoxide, 1 to the corresponding carbonyl ylide, 2.² Similar examples of valence isomerizations are observed in several other cyclic systems like cyclopropanones, 3,^{3,4} aziridines, 4,⁵ and diazirene imines, 5.⁶

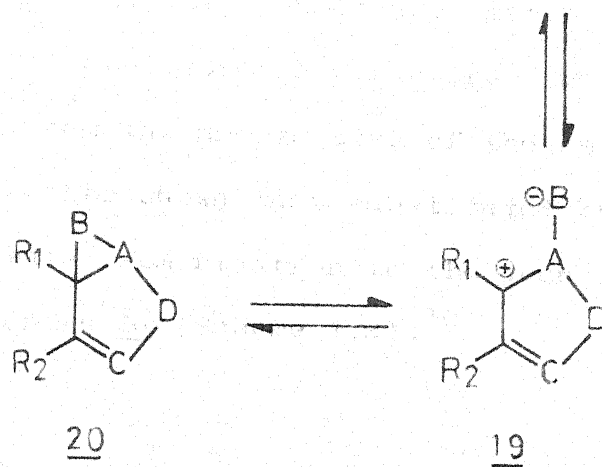
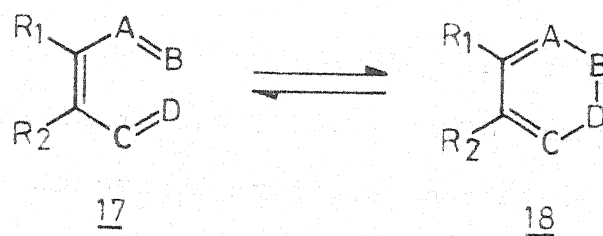
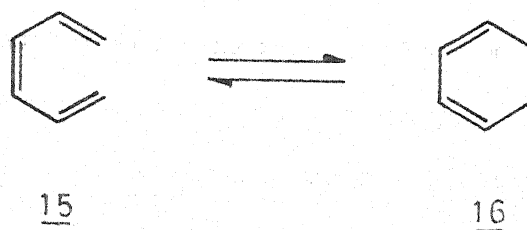
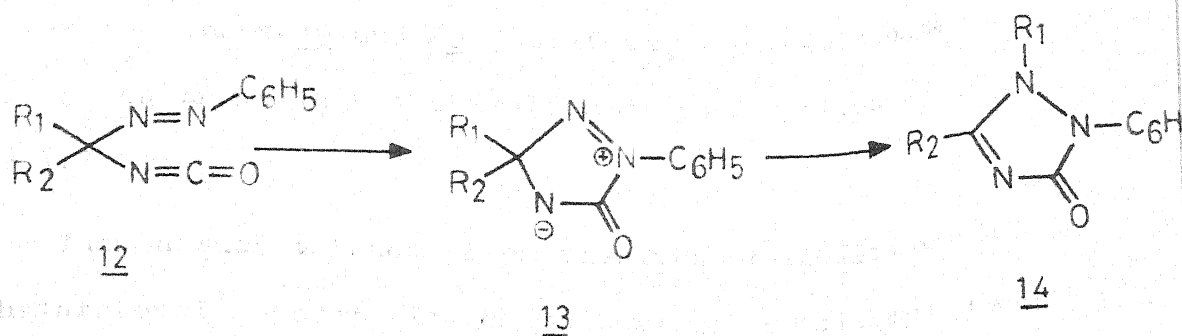
Maier⁷ has reported an interesting transformation of a dicarbonyl compound, 9 to a bifuran derivative, 11, which could be regarded as an example of valence isomerism involving four membered and five membered ring systems (Scheme 1.1). Another case of valence isomerism in a five membered ring is observed in the isomerisation of the α -phenylazoisocyanate, 12 to the 1,2,4-triazolidone, 14, through the possible intermediate, 13 (Scheme 1.1).⁸

Valence isomerisations of simple 1,3,5-hexatrienoids, 15, leading to the corresponding cyclohexadienes, 16, have been investigated in detail in carbon systems and the general nature of this type of transformations has long since been established. It is only natural to expect a similar type of general behaviour in hexatrienoids containing heteroatoms. In such systems, besides the hexatrienoid form, 17, and the cyclohexadienoid

Scheme 1.1



Scheme 1-1 (Contd.)



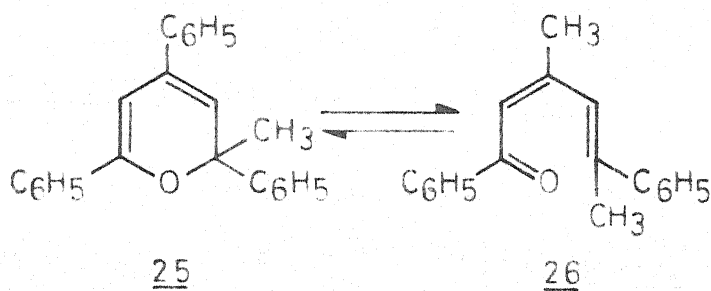
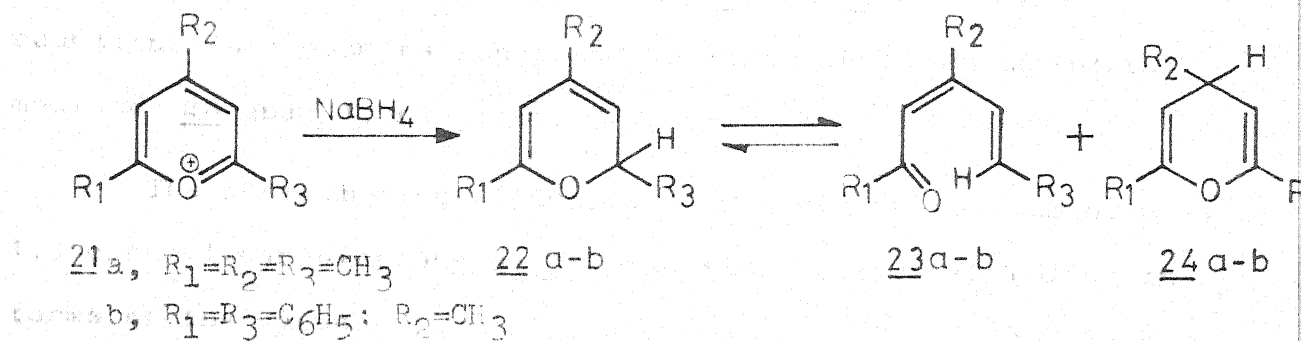
form, 18, one would expect a five membered, dipolar form such as, 19, as well as a bicyclo[3,1,0]hexene form such as 20, the latter two forms, 19 and 20 justifying their existence because of the aromatic stabilisation of such systems. (Scheme 1.1).

Though such valence isomerisation possibilities in heterohexatrienoid systems are quite obvious, no attempt has so far been made to explain a wide variety of interesting transformations of heterohexatrienoids reported in the literature in terms of their valence isomers. In the following pages, we have tried to explain some of the reactions of different types of heterohexatrienoids which are reported in the literature in terms of the valence isomers of these systems.

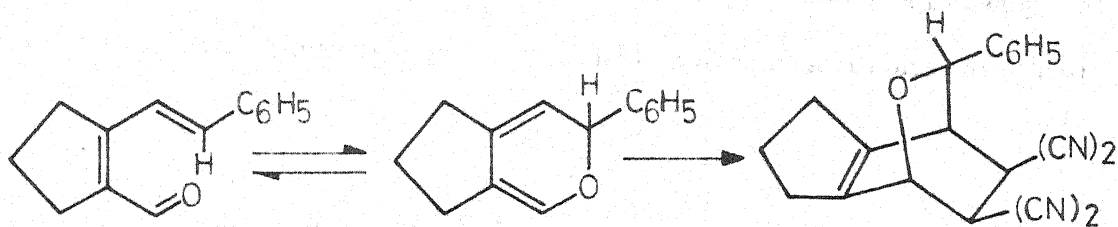
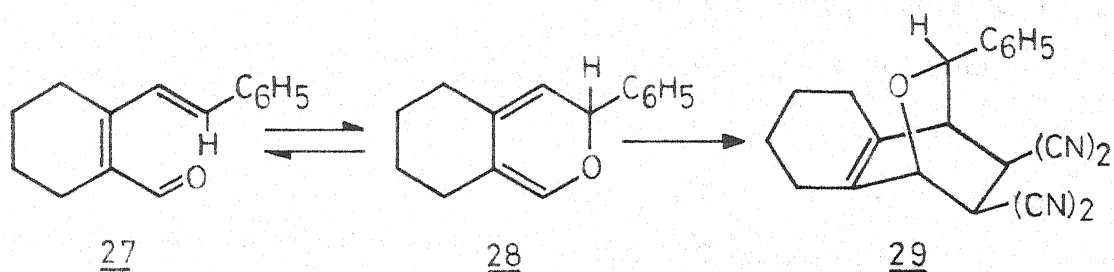
1.2 SYSTEMS WITH ONE HETERO ATOM

Marvel and coworkers have studied the sodium borohydride reduction of a pyrillium salt like, 21 at low temperatures and have shown that a mixture of products consisting of the ⁴H-pyran, 22, the 2H-pyran, 23 and the open-chain, dienone, 24, are formed.⁹ Evidence for the valence isomeric structures such as 23 and 24 has been obtained from the nmr spectra of the reaction mixture. These workers have also shown that substituted 2H-pyrans such as 25 undergo valence isomerisation to the corresponding open-chain dienones such as 26 (Scheme 1.2).¹⁰

Scheme 1.2



Scheme 1.3



Schiess and coworkers¹¹ have observed that conjugated dienaldehydes like 27 and 30 undergo cycloadditions with tetracyanoethylene to give products, 29 and 32 and these reactions have been rationalised in terms of 2H-pyran intermediates 28 and 31, respectively (Scheme 1.3).

The photochemical hydrolysis of pyridine to 4-aminobuta-1,3-diene-1-carboxaldehyde (36) can similarly be explained in terms of the valence isomeric intermediates like 34 and 35 (Scheme 1.4).¹²⁻¹⁴

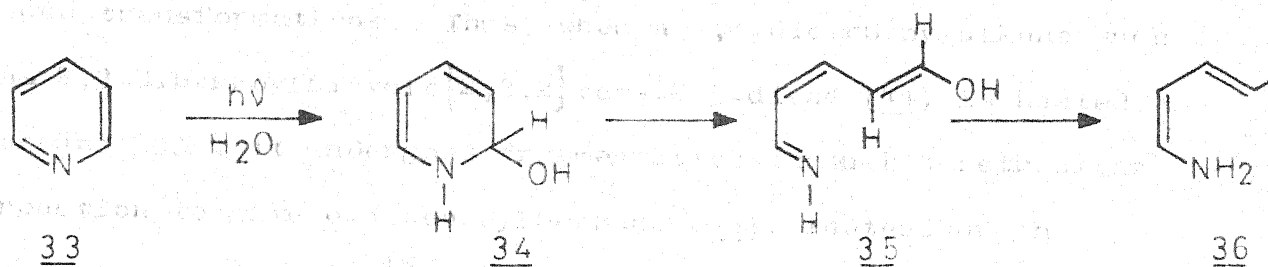
1.3 SYSTEMS CONTAINING TWO HETERO ATOMS

1.3.1 Systems with Two Oxygen Atoms

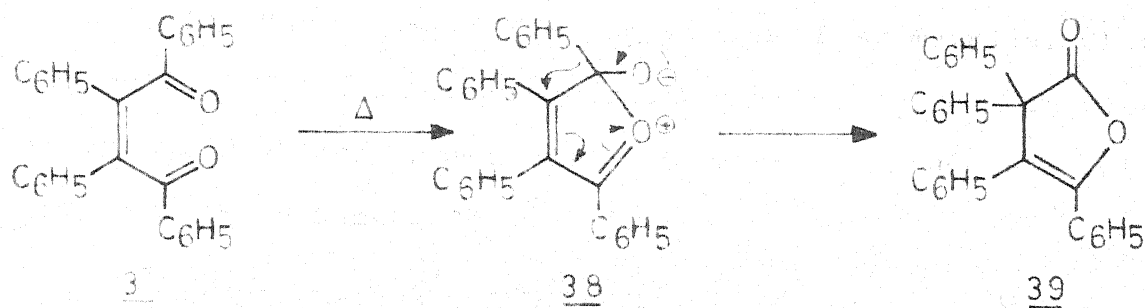
Zinin¹⁵ had reported that direct heating of 1,2-dibenzoyl-stilbene (37) gives rise to the tetraphenyl lactone, 39. A reasonable mechanism for this transformation would involve the initial valence isomerisation of 37 to the five-membered intermediate, 38 which would then rearrange to 39 (Scheme 1.5). Similarly, the existence of structures like 41 or 43 can be conveniently invoked to explain the ready deoxygenation of 1,4-dicarbonylalkenes to the corresponding furan derivatives 42, by phosphorous trihalides and trialkyl phosphites (Scheme 1.6).^{16,17}

In this context mention may be made of few limiting cases of reactions wherein such valence isomerisations are not

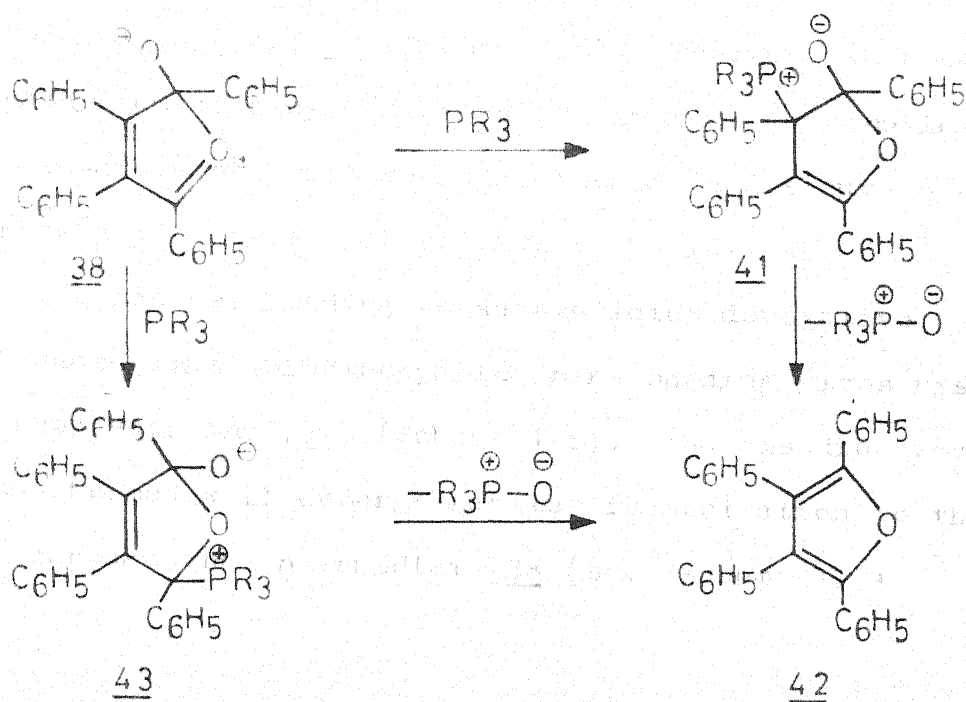
Scheme 1.4



Scheme 1.5



Scheme 1.6

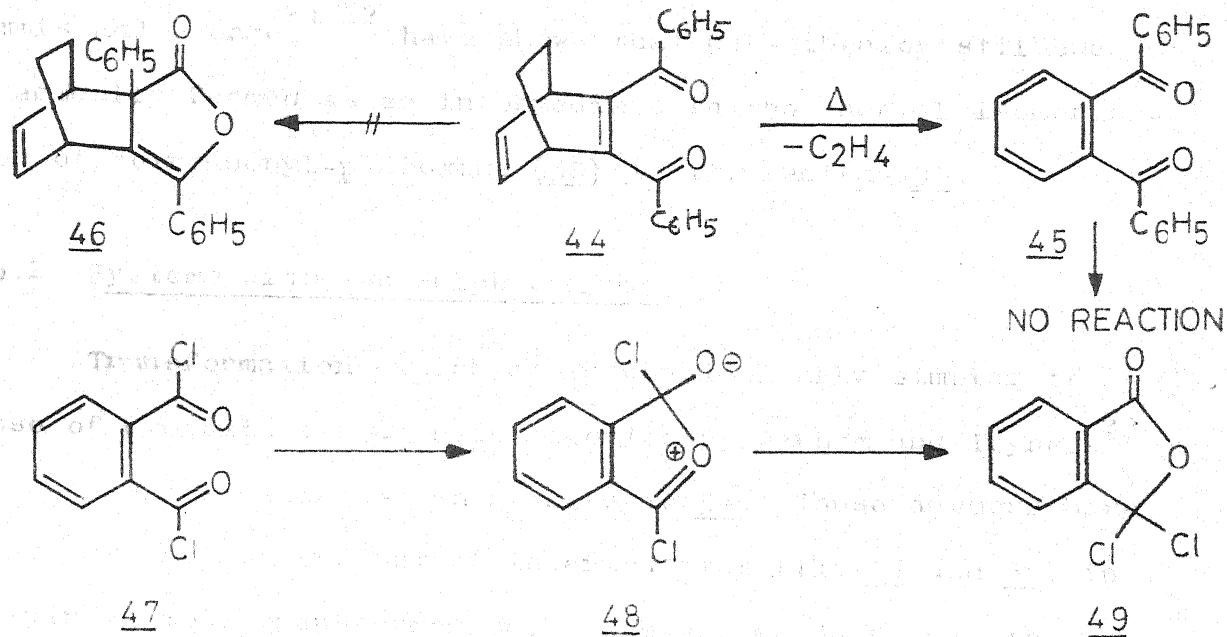


observed, although from their structural features one would expect such transformations. Thus, when a 1,4-dicarbonylalkene such as 2,3-dibenzoylbicyclo[2,2,2]octa-2,5-diene (44) is heated around 200°, it undergoes fragmentation through a retrodiene reaction to give *o*-dibenzoylbenzene (45), instead of the expected lactone 46.¹⁸ On the other hand, *o*-dibenzoylbenzene (45) which in itself is a 1,4-dicarbonylalkene does not undergo any change on heating under similar conditions.¹⁸

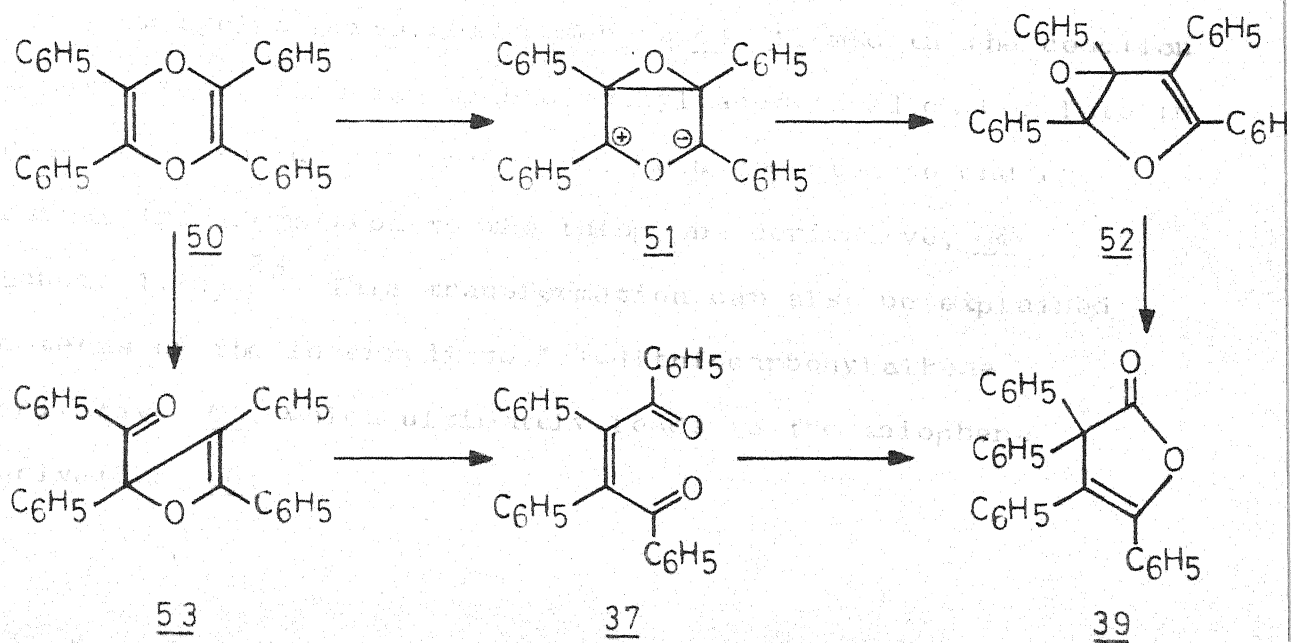
The known thermal isomerisation of symmetrical phthaloyl chloride (47) to its unsymmetrical isomer, 49, can be viewed as a case of valence isomerisation involving the dipolar intermediate 48 (Scheme 1.7).¹⁹

It has been shown by Berger and Summerbell²⁰ that the thermolysis of tetraphenyl-*p*-dioxine (50) results in the formation of the unsaturated lactone 39. These authors have suggested a mechanism for this transformation, involving intermediates like, 51 and 52 (Scheme 1.8). However, we feel that this transformation can be explained in terms of the intermediacy of *cis*-dibenzoylstilbene (37), formed in a sequence of symmetry allowed processes. These involve an initial $\sigma^2_s + \pi^2_s + \omega^2_s$ process leading to an oxetidine derivative, 53 which on subsequent electrocyclic ring opening gives rise to *cis*-dibenzoylstilbene (37) (Scheme 1.8). The *cis*-dibenzoylstilbene thus formed will undergo further isomerisation to the lactone 39, through the intermediate 38 (see, Scheme 1.5).

Scheme 1-7



Scheme 1-8



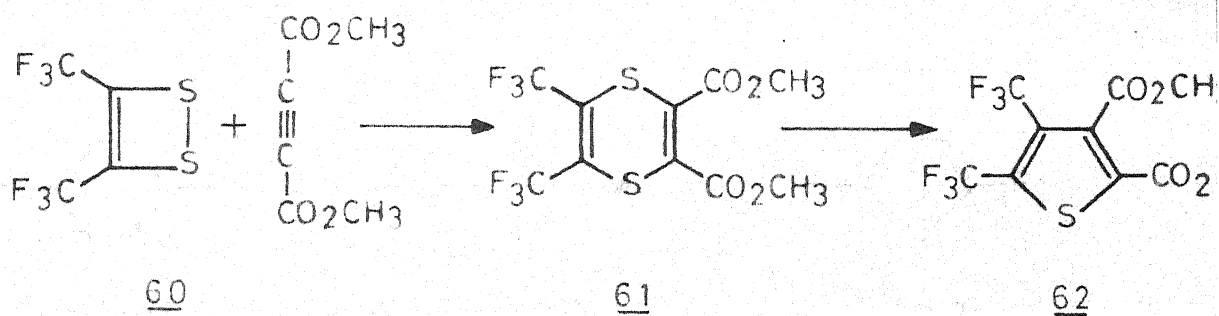
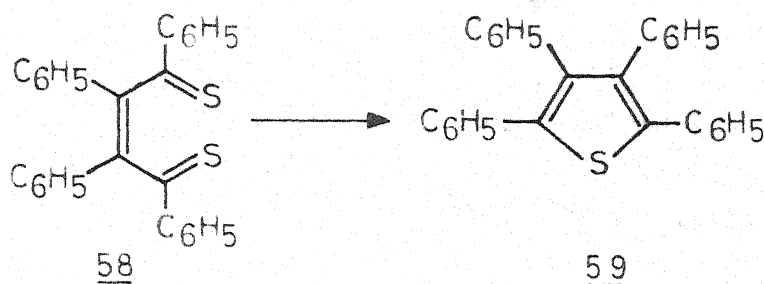
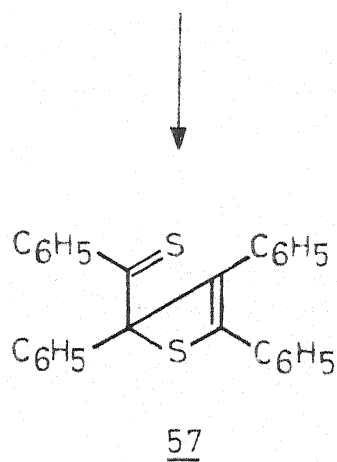
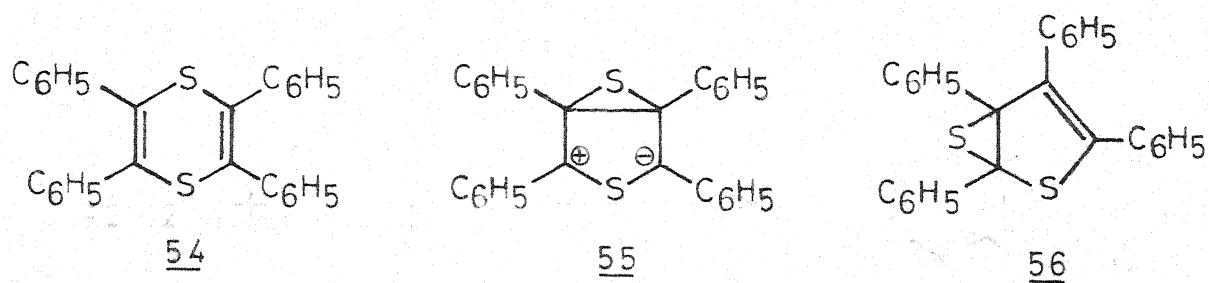
In this connection it might be mentioned that recently Jemmis and George^{21,22} have shown that cis-dibenzoylstilbene is actually formed as an intermediate in the thermal isomerisation of tetraphenyl-p-dioxine (50) to the lactone 39.

1.3.2 Systems with Two Sulphur Atoms

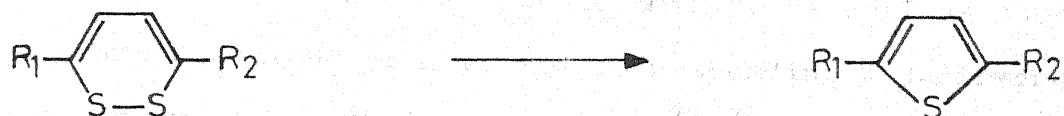
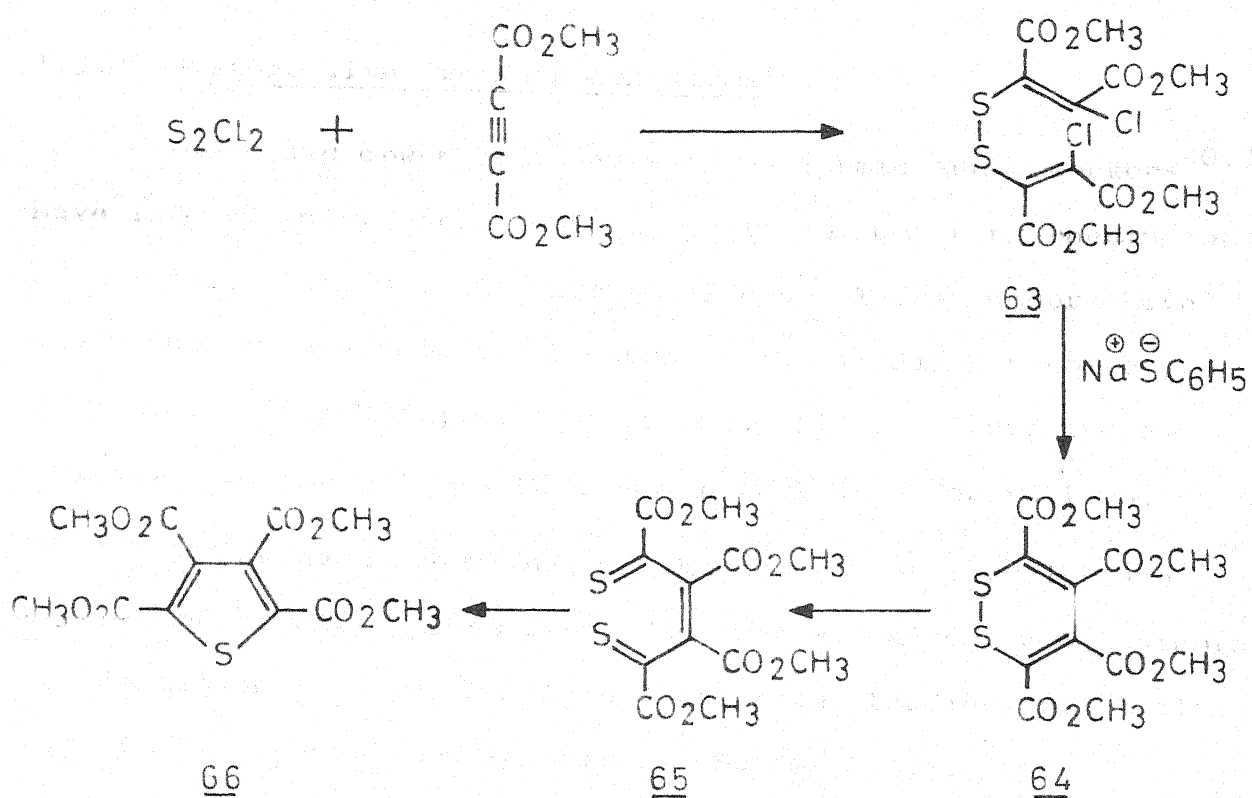
Transformations which are mechanistically similar to those of p-dioxines have been reported by Parham and Trynells²³ for the corresponding sulphur analogue, 54. These authors have suggested the involvement of intermediates like 55 and 56, in explaining this transformation. However, we feel that this reaction may very well be proceeding through cis-dithiobenzoylstilbene (58), which subsequently loses elemental sulphur to give the thiophene derivative, 59 (Scheme 1.9). A similar mechanism can be invoked to explain the formation of the thiophene derivative, 62 in the reaction of 60 with dimethyl acetylenedicarboxylate (Scheme 1.9).²⁴

A cyclic persulphide such as 64, formed in the reaction of sulphur monochloride with dimethyl acetylenedicarboxylate in presence of sodium mercaptide has been reported to undergo thermal transformation to the thiophene derivative, 66 (Scheme 1.10).²⁵ This transformation can also be explained in terms of the intermediate 1,4-dithiocarbonylalkene derivative, 65, which ultimately leads to the thiophene derivative, 66.

Scheme 1-9



Scheme 1.10



67 a, $\text{R}_1 = \text{CH}_3 - \text{C} \equiv \text{C}$; $\text{R}_2 = \text{C} \equiv \text{C} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$

b, $\text{R}_1 = \text{CH}_3 - \text{C} \equiv \text{C}$; $\text{R}_2 = (\text{C} \equiv \text{C})_2 - \text{CH} = \text{CH}_2$

c, $\text{R}_1 = \text{CH}_3 - (\text{C} \equiv \text{C})_2$; $\text{R}_2 = \text{C} \equiv \text{C} - \text{CH} = \text{CH}_2$

68 a-c

An analogous transformation has been observed by Bohlmann and coworkers²⁶⁻²⁸ who have shown that some naturally occurring, sulphur containing polyacetylenes such as 67 are easily converted to their corresponding thiophene derivatives 68 (Scheme 1.10).

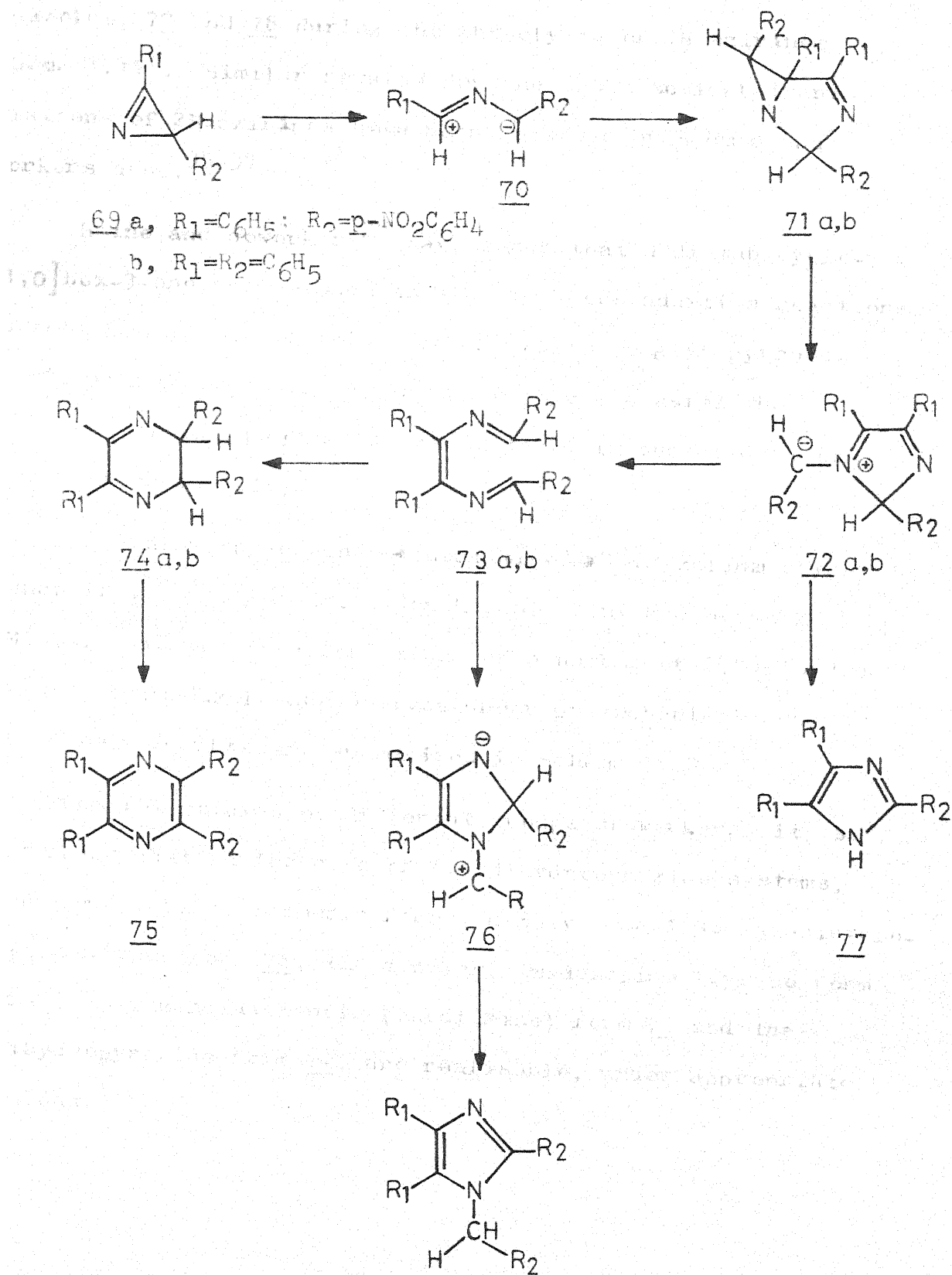
1.3.3 Systems with Two Nitrogen Atoms

Padwa and coworkers²⁹, as well as Schmid and coworkers^{30,31} have independently shown that the photochemical ring opening of 2H-azirines gives rise to nitrile ylides. These authors have shown that in presence of electron deficient dipolarophiles, such photochemically generated nitrile ylides undergo cycloaddition reactions to pyrrole and pyrrolidine derivatives.

It has been shown that in the absence of any dipolarophile, the nitrile ylides from 2H-azirines, undergo a 1,3-dipolar cycloaddition to a ground state 2H-azirine, leading to 1,3-diazabicyclo[3,1,0]hex-3-ene systems 71 (Scheme 1.11).³²

Earlier, Padwa and coworkers had shown that 1,3-diazabicyclo[3,1,0]hex-3-ene systems 71 undergo ring opening reactions to give the corresponding heterotrienoids, 73.³³ These enediimines, 73 have been shown to undergo photochemical, as well as thermal ring closure reactions to give the corresponding 2,3-dihydropyrazine derivatives, 74 (Scheme 1.11).^{33,34} The opening of the three-membered ring of the diazabicyclo[3,1,0]hex-3-ene, 71, as well as an alternative valence isomerisation of the enediimine, 73 both leading to the dipolar, imidazolium ylides

Scheme 1-11



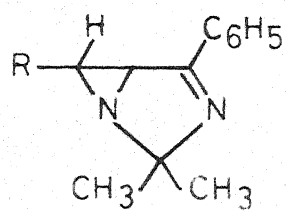
72 or 76 have been invoked to explain the formation of imidazoles, 77 and 78 during the photolysis of 2H-azirines (Scheme 1.11). Similar results for the photochemical transformations of 2H-azirines have been reported by Schmid and coworkers also.³⁵⁻³⁷

Heine and coworkers³⁸ have shown that a diazabicyclo-[3,1,0]hex-3-ene system such as 71, undergoes addition reactions with acetylenic and olefinic dipolarophiles to give pyrrolo-[1,2-c]imidazoles 79 and 80, and they have suggested the involvement of the dipolar intermediate 72 in these addition reactions (Scheme 1.12).

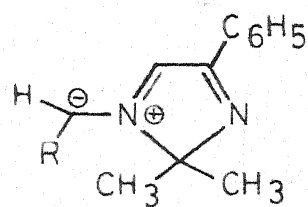
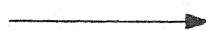
A 2,3-dihydropyrazine \rightarrow enediimine \rightarrow imidazolium ylide sequence of valence isomerisation has been invoked by Beak and Miesel³⁹ in the transformations of a number of 2,3-dihydropyrazines to imidazole derivatives under photochemical conditions. Their results are summarised in Scheme 1.13.

From the studies of different groups of workers, it is fairly clear that in the case of 2,3-dihydropyrazine systems, all the four valence isomeric forms, namely, the 1,3-diazabicyclo-[3,1,0]hex-3-ene form 71, the dipolar, imidazolium 1-ylide form 72, the 2,4-diazahexatrienoid (enediimine) form 73 and the 2,3-dihydropyrazine form 74, are realisable, under appropriate conditions.

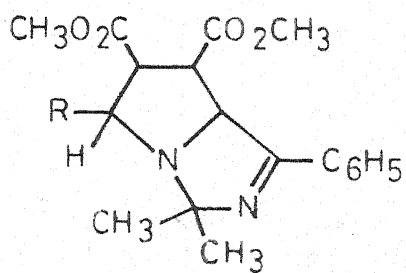
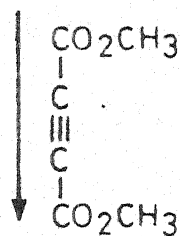
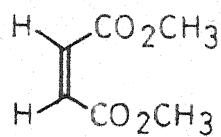
Scheme 1-12



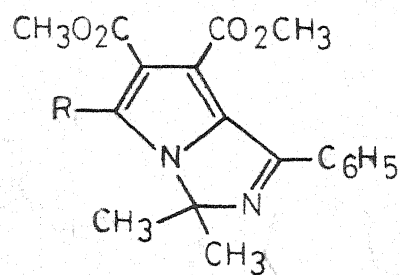
71



72



80



79

1.3.4 Systems with One Oxygen and One Nitrogen Atoms

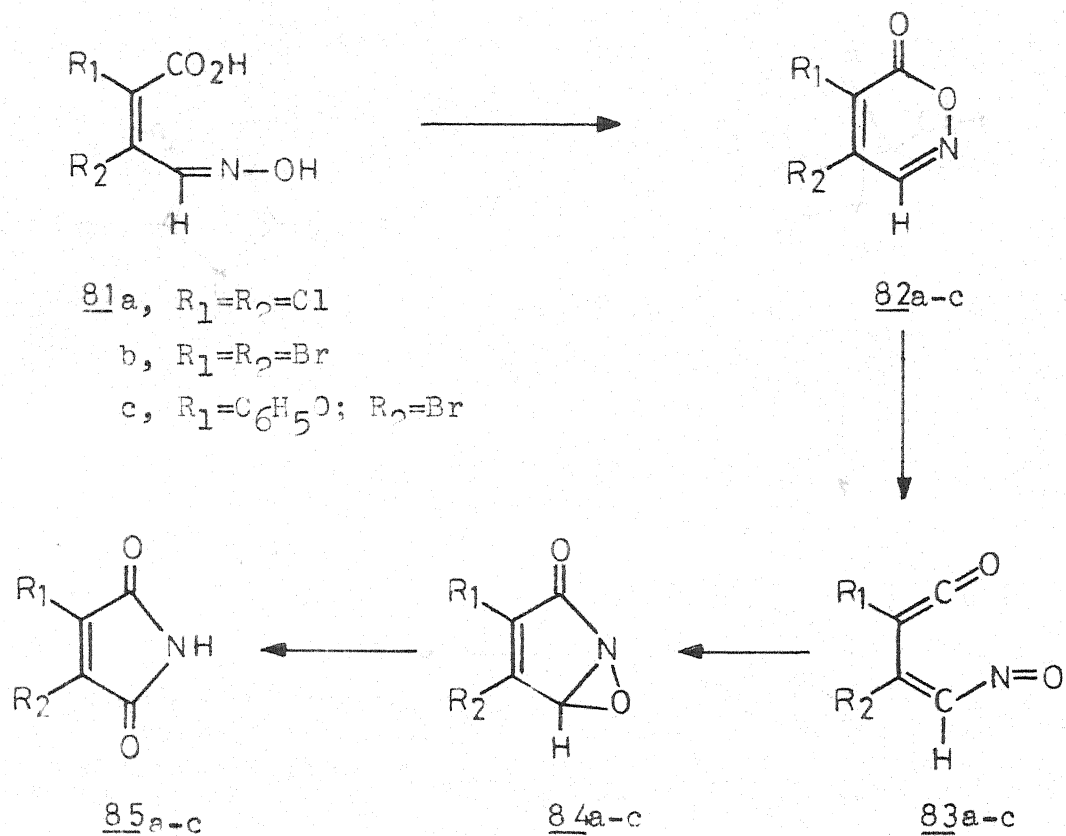
A number of derivatives of 1,2-oxazines are reported in the literature. A few interesting transformations of 1,2-oxazine derivatives which could be explained through valence isomeric intermediates are discussed here.

1,2-Oxazine-6-ones, 82, formed from the oximes of maleic acid monoaldehydes are known to thermally rearrange to the corresponding maleimides, 85.⁴⁰⁻⁴² A probable route to the formation of 85 involves intermediates like 82-84 (Scheme 1.14).

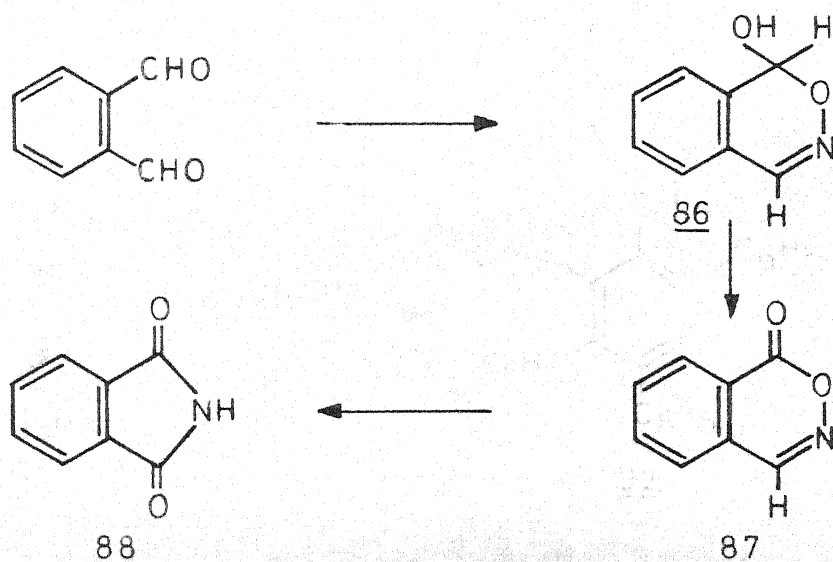
The rearrangement of oxime anhydrides (1,2-oxazine-6-ones) to the corresponding dicarboxylic acid imides appears to be a general reaction. Thus, when phthalaldehyde is heated with hydroxylamine, benzo[d]-1,2-oxazine-6-ol (86) is formed which upon oxidation gives the corresponding 1,2-oxazine-6-one, 87. Thermal rearrangement of 87 to phthalimide, 88, can be rationalised in terms of valence isomeric intermediates, analogous to 82, 83, and 84.

Dilthey and Passing^{44,45} had reported that the reaction of nitrosobenzene with tetraphenylcyclopentadienone (89) leads to the formation of the unsaturated lactam, 94 (Scheme 1.16). In a reinvestigation of this reaction, Ranganathan and Kar⁴⁶ have shown that the reaction of nitrosobenzene with tetraphenylcyclopentadienone gives the cycloadduct, 90, which on subsequent

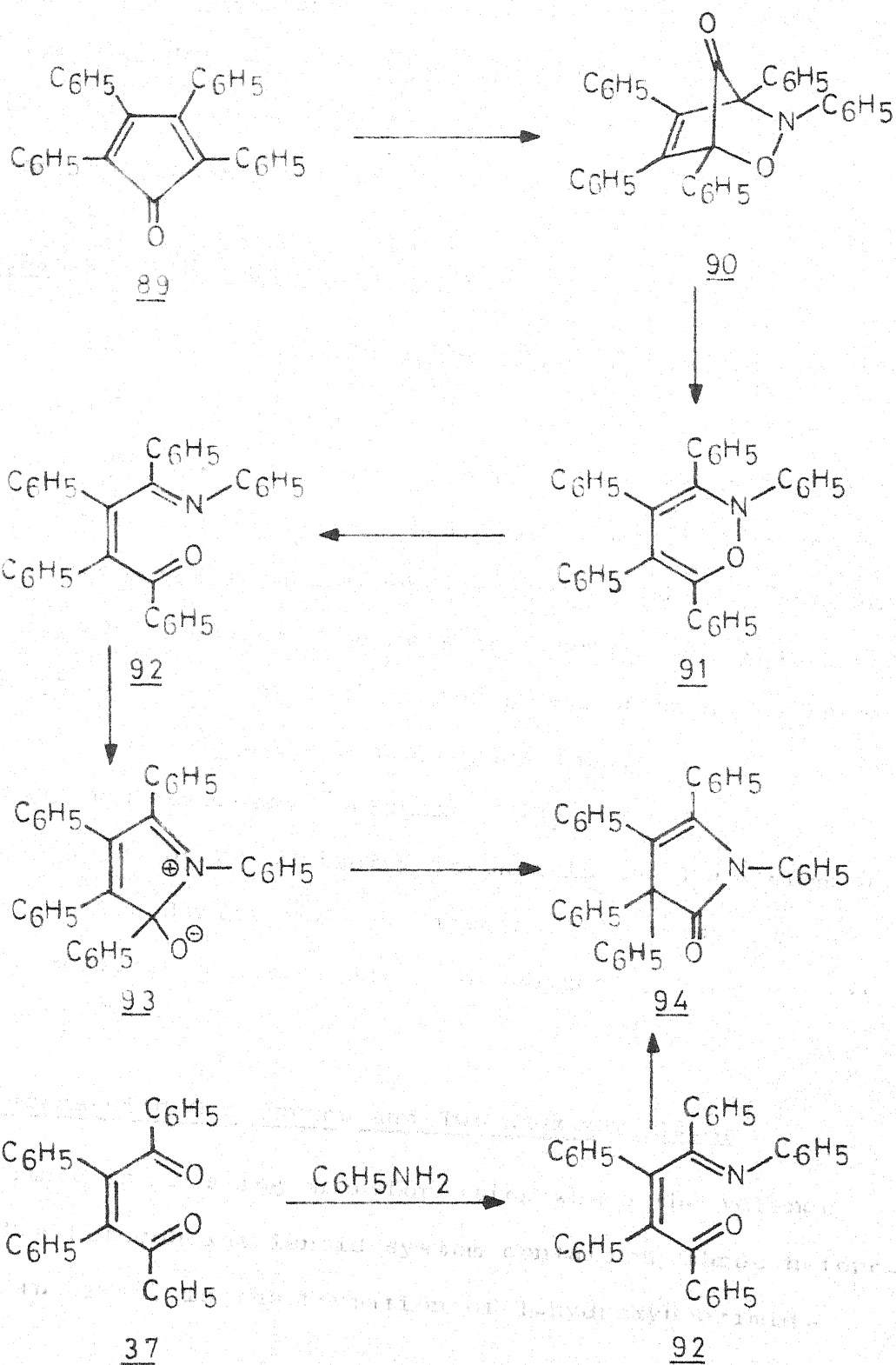
Scheme 1-14



Scheme 1-15



Scheme 1-16



decarbonylation gives the oxazine derivative 91. Valence isomerisation of 91 has been invoked to explain the formation of the lactam 94. Similarly the formation of the lactam, 94, in the reaction of cis-dibenzoylstilbene (37) with aniline can be rationalized in terms of valence isomeric intermediates like 92 and 93 (Scheme 1.16).⁴⁷

1.4 SYSTEMS WITH THREE HETERO ATOMS

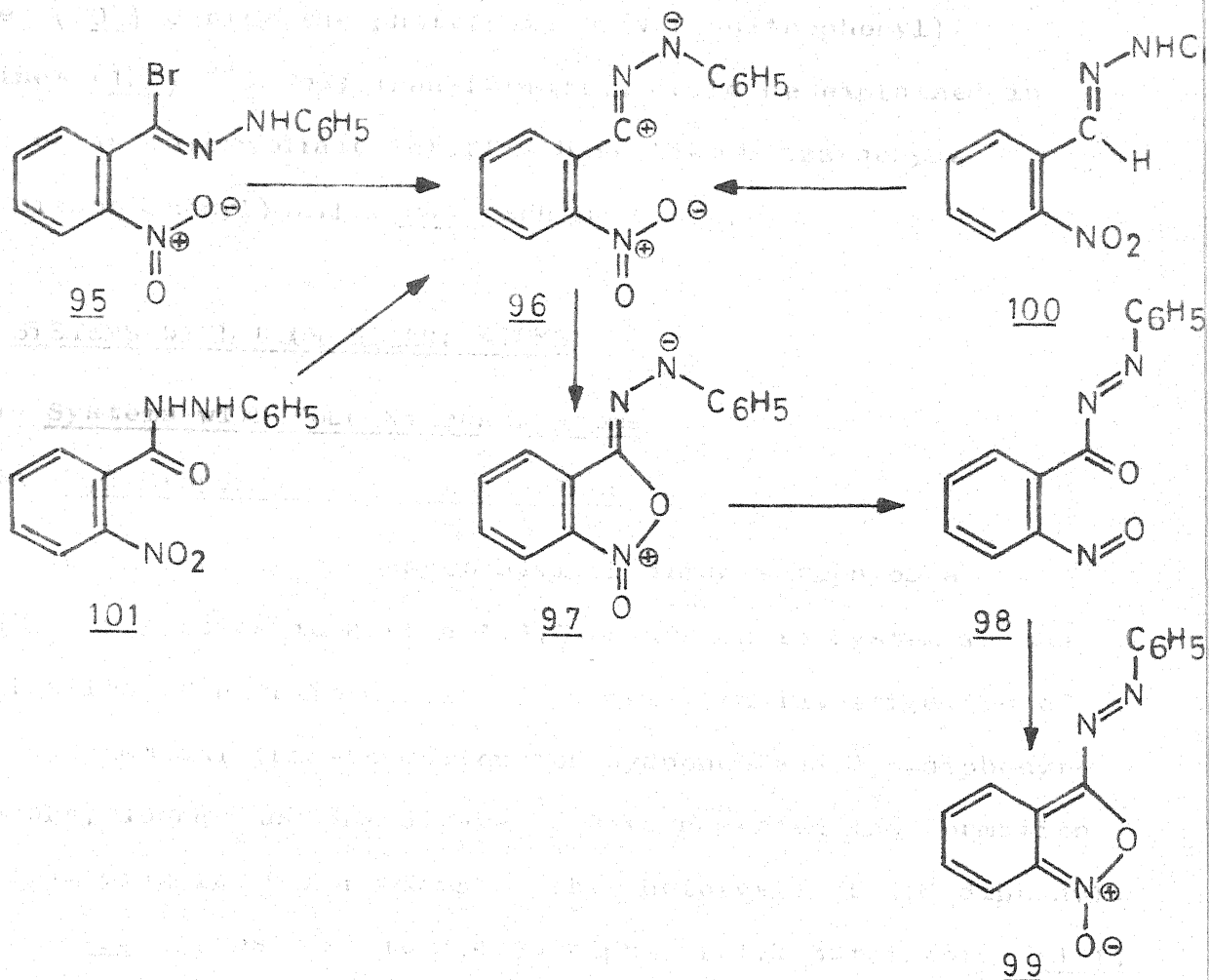
1.4.1 Systems with One Nitrogen and Two Oxygen Atoms

Gibson⁴⁸ had reported that N-phenyl-C-(o-nitrophenyl)-nitrileimine (96) exists as the isomeric phenylazoanthranil-N-oxide (99) (Scheme 1.17). This could be cited as an example of valence isomerism in a heterohexatrienoid system, containing three heteroatoms. Valence isomers of anthranil-N-oxide, such as 97 and 98 might be involved in the preparation of anthranil-N-oxides from phenyl-o-nitrobenzoylhydrazines, 101, as reported by Chattaway and coworkers⁴⁹ (Scheme 1.17). Structures like 96, 97 and 98 can be conveniently invoked in the formation of anthranil-N-oxide during the lead tetraacetate oxidation of phenylhydrazones of o-nitroaromatic aldehydes such as 100, also (Scheme 1.17).⁵⁰

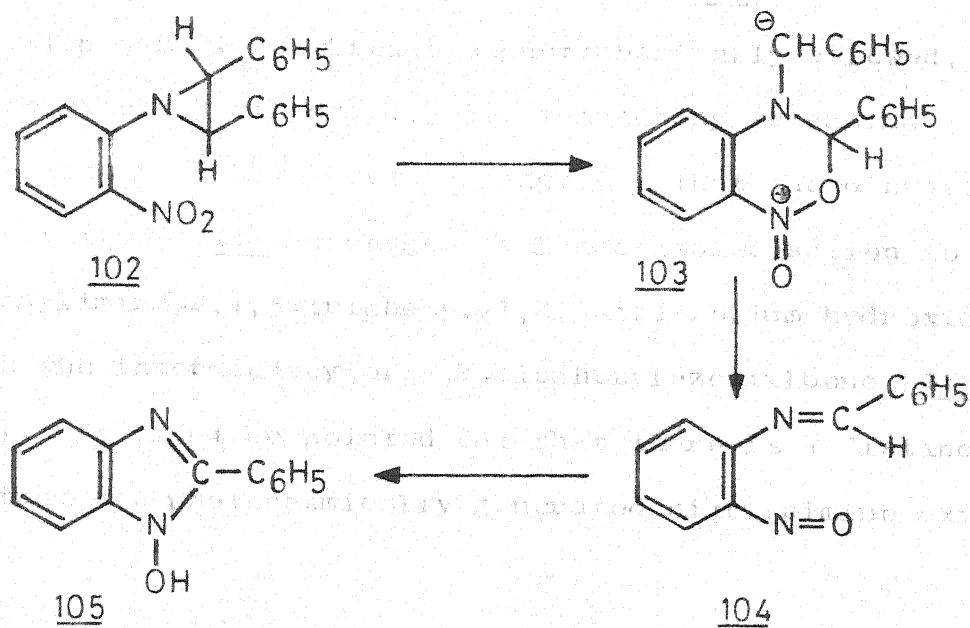
1.4.2 Systems with One Oxygen and Two Nitrogen Atoms

Another interesting transformation where the valence isomers of a heterohexatrienoid system containing three heteroatoms are involved, is the formation of 1-hydroxybenzimid-

Scheme 1.17



Scheme 1-18



azoles (105) during the photolysis of N-(o-nitrophenyl)-azirines (102).⁵¹ This transformation could be explained in terms of an intermediate Schiff's base like benzaldehyde N-(o-nitrosophenyl)anil (104) (Scheme 1.18).

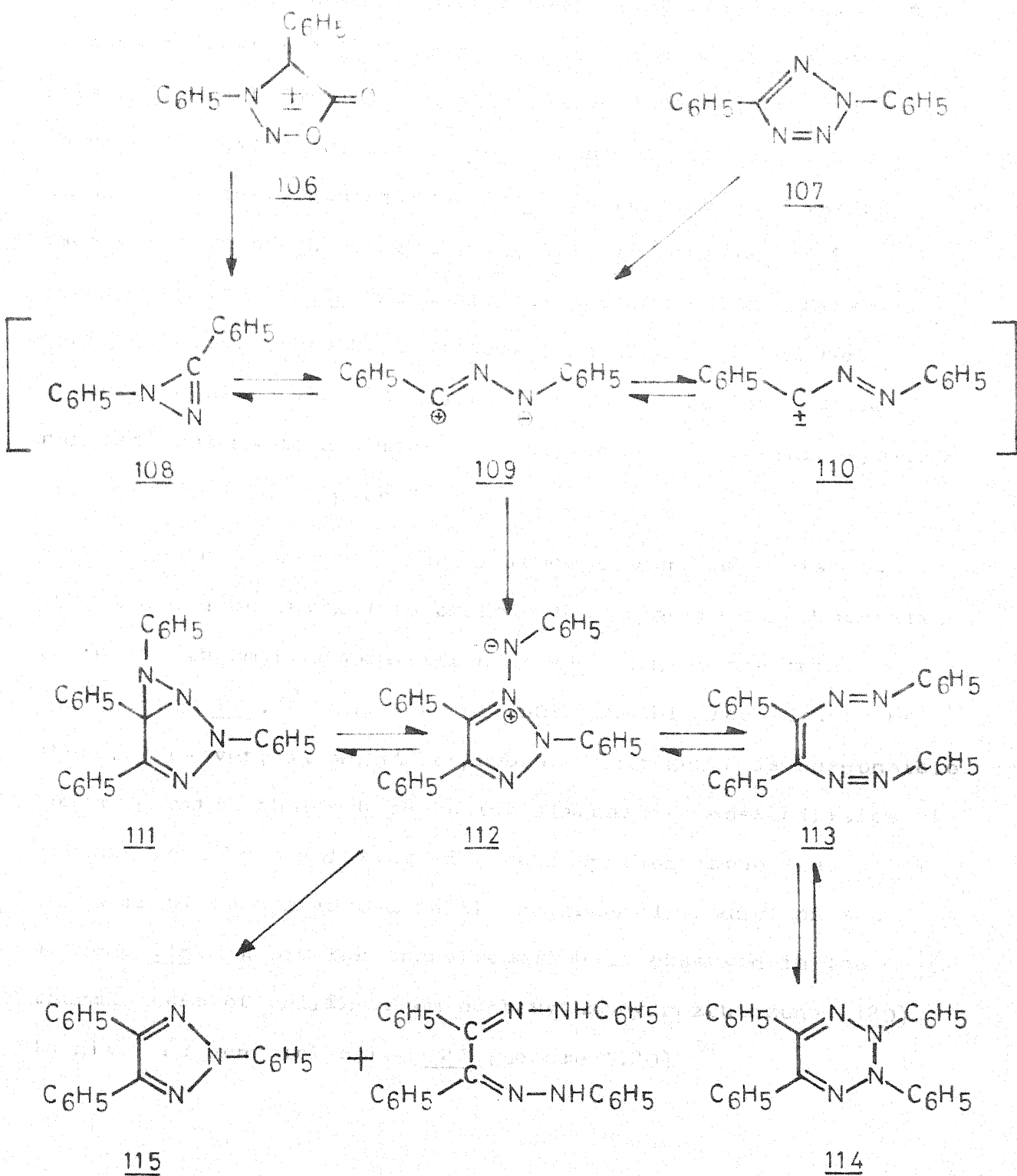
1.5 SYSTEMS WITH FOUR HETERO ATOMS

1.5.1 Systems with Four Nitrogen Atoms

1.5.1a 2,3-Dihydro-1,2,3,4-tetrazines

An example of the photochemical dimerisation of a 1,3-dipolar species to give a 1,3,5-hexatrienoid system is the dimerisation of nitrileimines. In a detailed investigation of the photochemical transformations of sydnones and 2,5-diphenyl-tetrazole, George and Angadiyavar⁵² have reported the formation of 1,2,3-triazoles. For example, the photolysis of N,C-diphenylsydnone (106) gives rise to 2,4,5-triphenyl-1,2,3-triazole (115). It has been suggested that N,C-diphenylsydnone undergoes an initial transformation to diphenylnitrileimine (109) which in a subsequent step dimerises through a photochemically allowed, 4+4 process to give 2,3-dihydro-2,3,5,6-tetraphenyltetrazine (114). These authors⁵² have further suggested that the dihydro-tetrazine derivative, 114 undergoes valence isomerisation to anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide (112) through the intermediacy of 1,2-bisphenylazostilbene (113) (Scheme 1.19). It might be pointed out that there is a distinct possibility that the photochemically generated nitrileimine exists

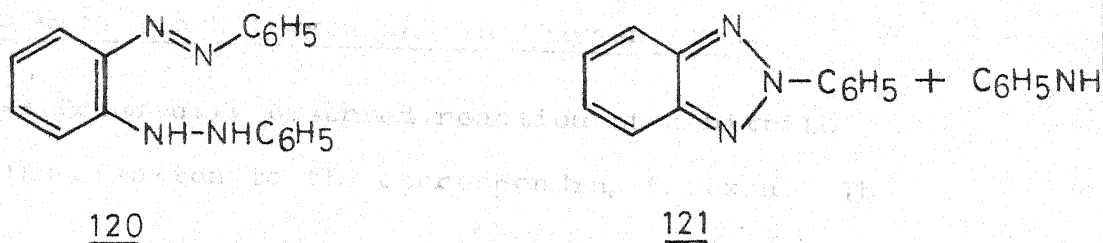
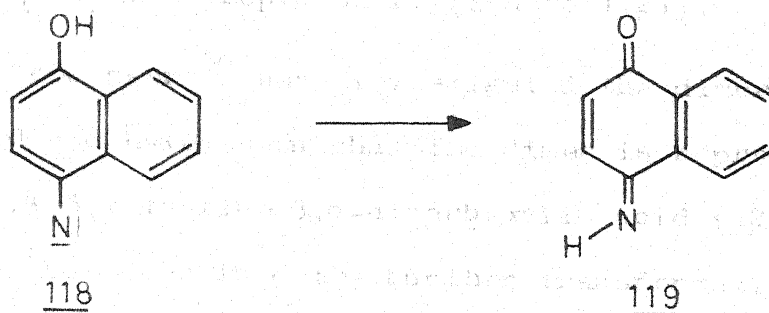
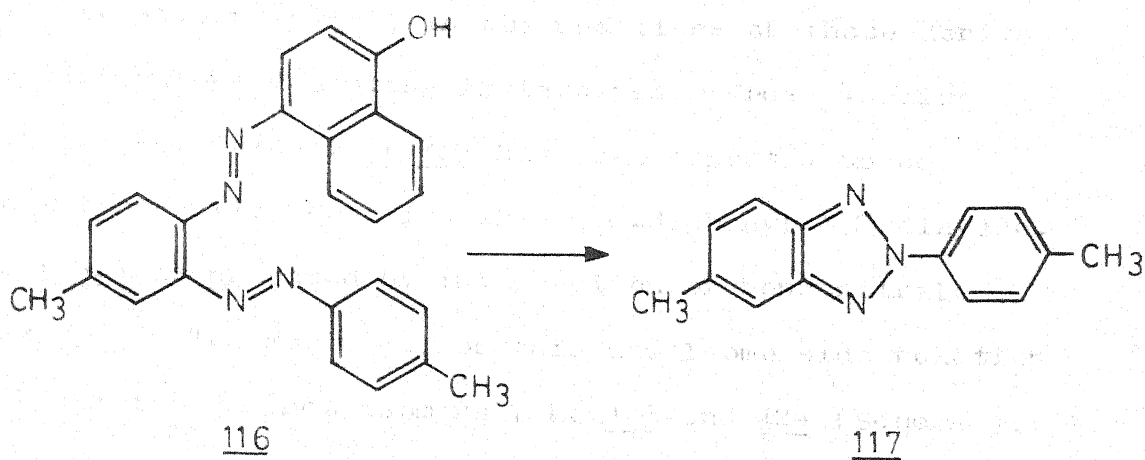
Scheme 1.19



as the phenyl phenylazocarbene (110) which could dimerise to give the bisphenylazostilbene (113). On the other hand, the formation of the anhydro iminotriazolium hydroxide, 112, can also be through a 1,3-dipolar cycloaddition of the nitrile-imine, 109 with itself. An alternative formulation would involve the cycloaddition of 109 to one of its valence isomers, namely, diphenyl-2H-diazirine (108) followed by the valence isomerisation of the cycloadduct, 111, to give 102. The transformation of 112 and analogous systems to the triazole derivatives, 115 has been discussed in detail in Chapter 2 of this thesis. The 1,3-dipolar cycloadditions of 112 and related systems to a number of acetylenic and olefinic systems are discussed in Chapter 3.

Another instance where valence isomers of a bisazo-alkene could be invoked to explain the experimental observations is in the thermal fragmentation of 116 to give the triazole derivative, 117.⁵³ The role of SnCl_4 in this reaction is not clear. However, it might be probable that SnCl_4 is responsible for a specific choice between two alternative possibilities of nitrene loss by complexing with the naphthoquinoneimine (119) which might be considered as the rearranged product of the nitrene 118. A similar transformation is observed in the thermal loss of aniline from *o*-phenylazohydrazobenzene (120) to give the benzotriazole, 121 (Scheme 1.20).⁵⁴

Scheme 1.20



1.5.1b 1,2-Dihydro-1,2,4,5-tetrazines

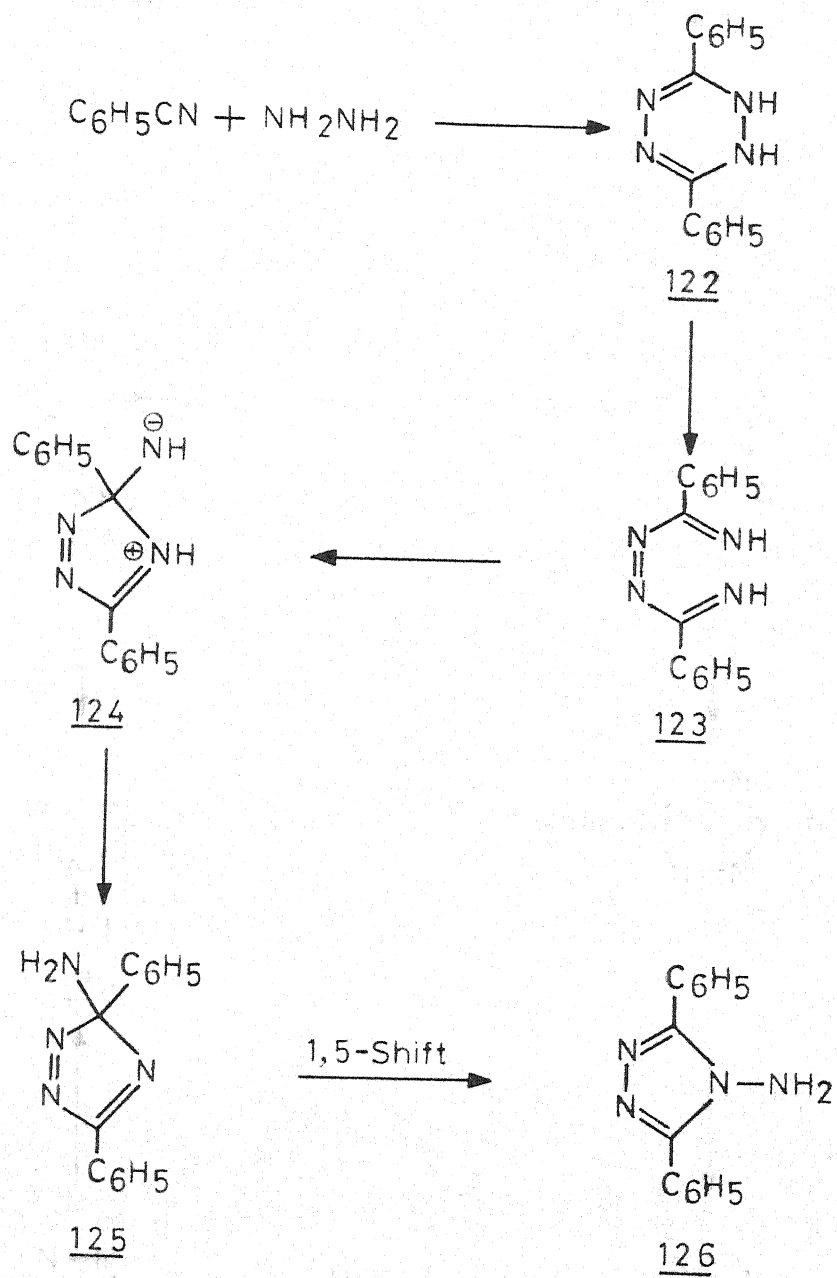
The thermal conversion of 1,2-dihydro-1,2,4,5-tetrazines to the 4-amino-1,2,4-triazoles has long since been recognised as an unavoidable side reaction, in the reactions of these derivatives wherein prolonged heating is involved. Thus, 4-amino-2,5-diphenyl-1,2,4-triazole (126) has been reported to be formed in a consecutive reaction when 3,6-diphenyl-1,2-dihydro-tetrazine (112) is prepared by the reaction of benzonitrile and hydrazine.⁵⁵ The mechanism of this unwelcome side reaction could also involve valence isomers like 123 and 124 (Scheme 1.21). The final conversion of the 3-amino-1,2,4-triazole derivative, 125, to the 4-amino-1,2,4-triazole, 126, would involve a symmetry allowed, [1,5] sigmatropic shift (Scheme 1.21).

Curtius and coworkers⁵⁶ have investigated the dimerisation of diazoacetic acid and have shown that the dimer is represented as 1,2-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid (127). These authors have also described the further transformation of this derivative to the aminotriazole derivatives, 128 and 129 through the sequence of reactions shown in Scheme 1.22. These transformations can be explained in terms of the valence isomers of dihydrotetrazine derivatives, 127 and 130.

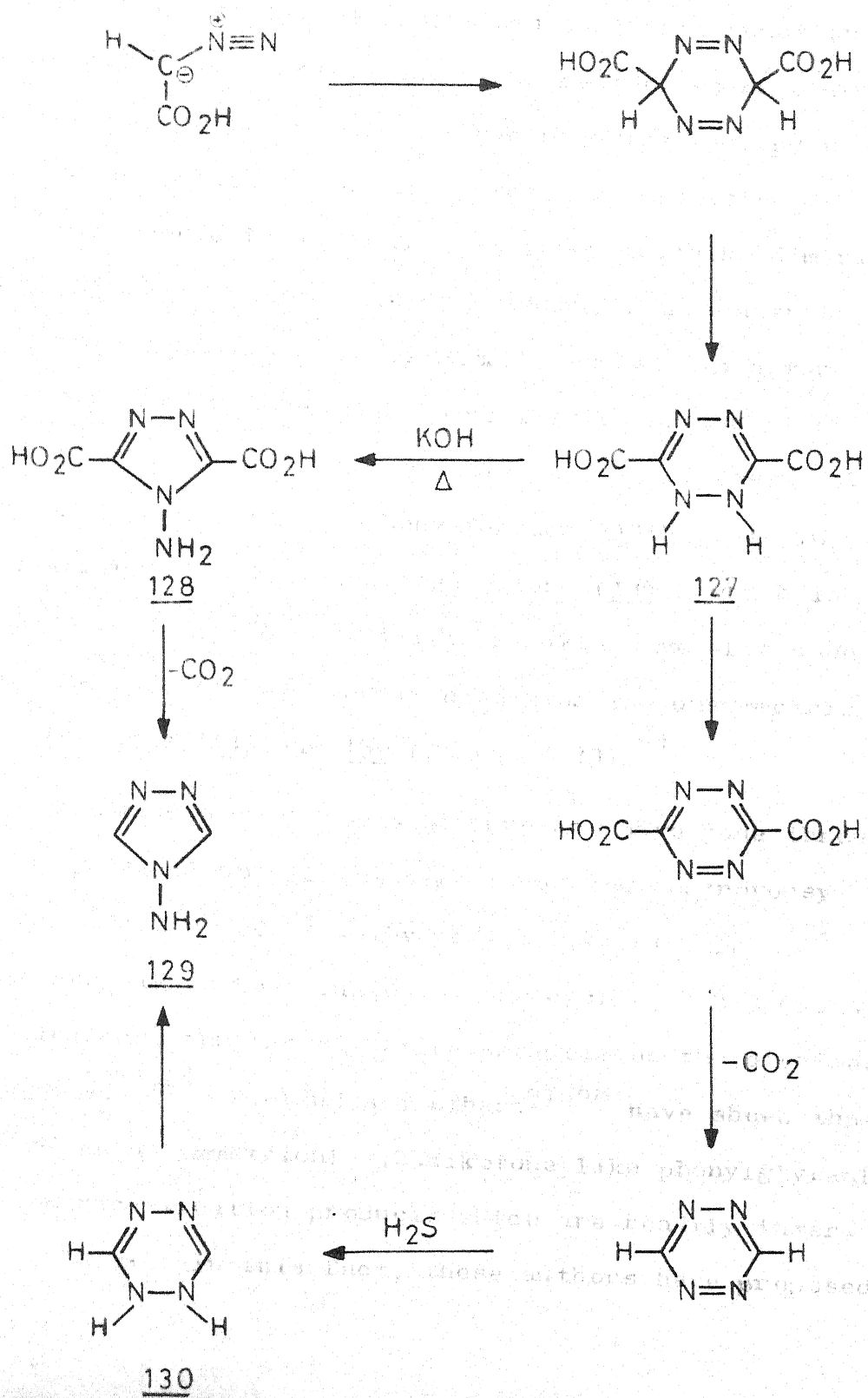
1.5.2 Systems with Two Nitrogen and Two Oxygen Atoms

The most frequently observed reaction of a nitrile oxide is its dimerisation to the corresponding furoxan. The

Scheme 1.21



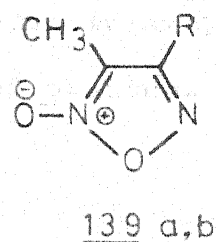
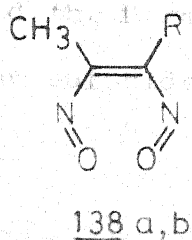
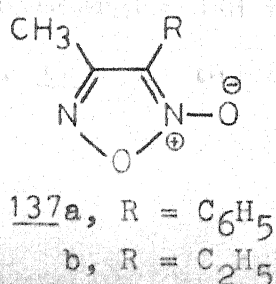
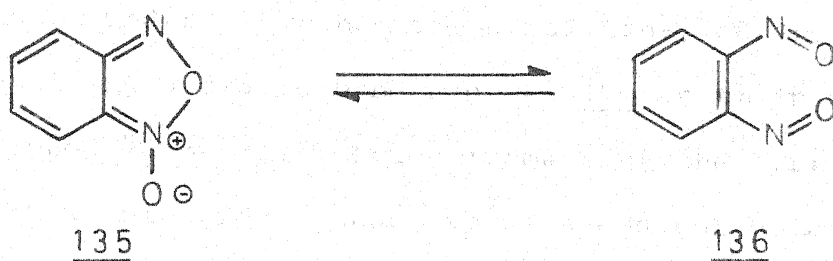
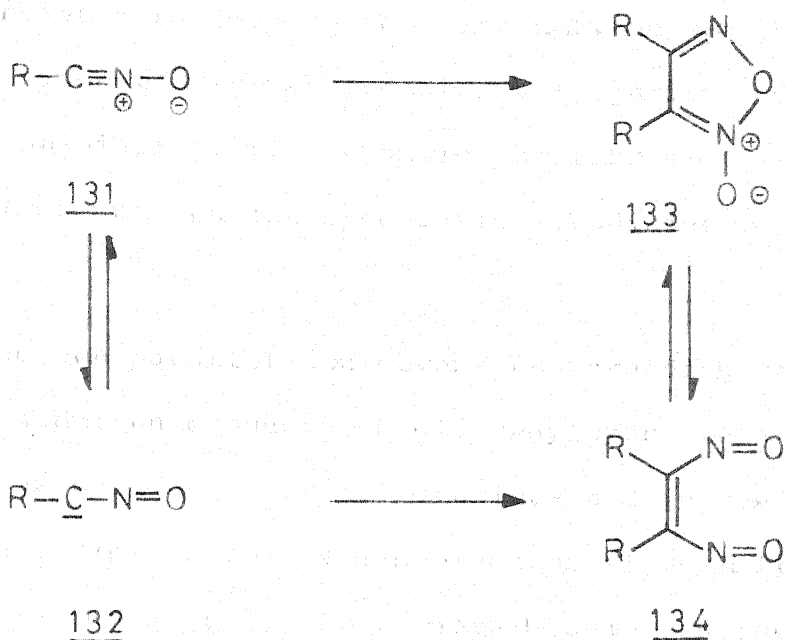
Scheme 1.22



dimerisation in most cases occur readily during the formation of the nitrile oxide itself. Kinetic studies on the dimerisation of several nitrile oxides have shown that this reaction follows a second order kinetics and is characterised by a low energy of activation, as well as a large negative entropy of activation, as one would expect in typical cycloaddition reactions.^{57,58} Hence it has been postulated that the dimerisation is essentially a 1,3-dipolar cycloaddition of a nitrile oxide (131) to another molecule of nitrile oxide. An alternative mode of reaction would involve the dimerisation of the nitroso-carbene, 132 to give the 1,2-dinitrosoolefine, 134 (Scheme 1.23). Nmr studies have shown that the benzofuroxan, (135) exists in mobile equilibrium with 1,2-dinitrosobenzene (136), which is a valence isomer of 135.⁵⁹⁻⁶¹ Similar results have also been reported in the case of equilibration between the unsymmetrically substituted furoxans, 137 and 139 (Scheme 1.23).⁶¹

The structural formulations of furoxans have gone through a controversy parallel in all its aspects of the controversy regarding the structure of 2,3-dihydro-1,2,3,4-tetrazines.⁶² Thus, Angeli and others have suggested the cyclic, 1,2,3,6-dioxadiazine structure for the oxidation products of the dioximes of 1,2-diketones.⁶³⁻⁶⁶ Wieland and others^{67,68} have shown that the dioxime of an unsymmetrical 1,2-diketone like phenylglyoxal gives two isomeric oxidation products which are readily interconverted. To explain this fact, these authors have proposed

Scheme 1.23



the furoxan structure for the oxidation product of 1,2-dioximes. The interconversion of the two isomeric products has been explained in terms of a 1,2-dinitrosoalkene intermediate.⁶⁹

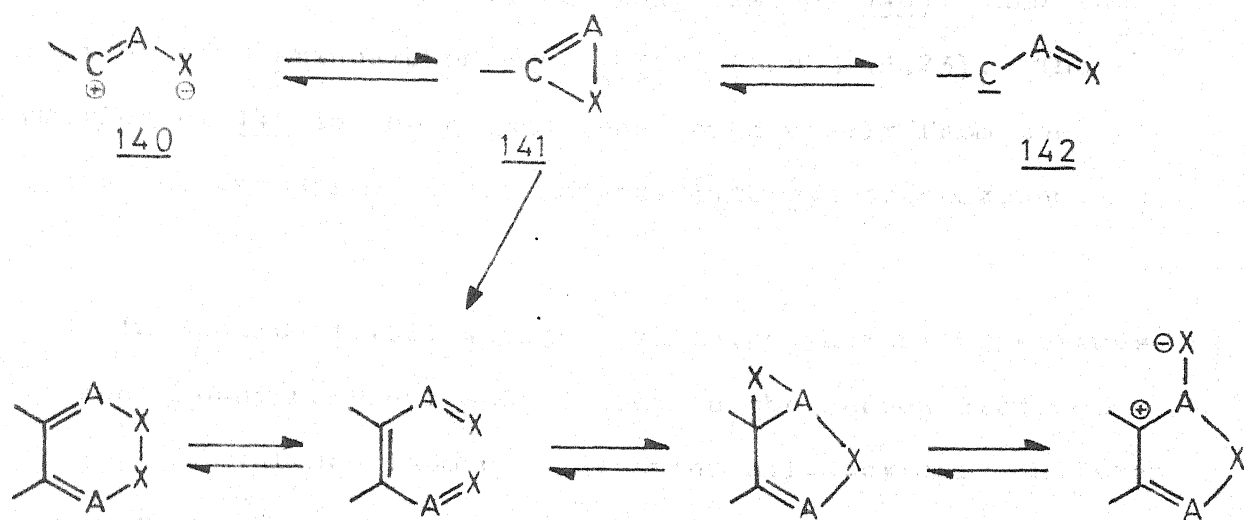
The furoxan structure is the currently accepted structure for these products though recent investigations have suggested the possibility of a dynamic equilibrium between the furoxan structure and the open chain 1,2-dinitrosoalkene form.⁵⁹⁻⁶¹

From the two parallel controversies regarding the structures of the oxidation products of bisphenylhydrazones of 1,2-diketones as well as their 1,2-dioximes and in the light of our results on the thermal and photochemical transformations of bisazoalkenes (Chapter 2), it is possible to conclude that the valence isomerisation between structures 17-20, is a general behaviour. This view is further substantiated by the photochemical transformations of pyrazines.³²⁻³⁹ The dimerisation, at least under photochemical conditions, of dipolar species containing a double bond such as 140 or their valence isomers, 141 and 142 to the valence isomers of the corresponding 1,3,5-heterohexatrienoids appears to be a general behaviour (Scheme 1.24).

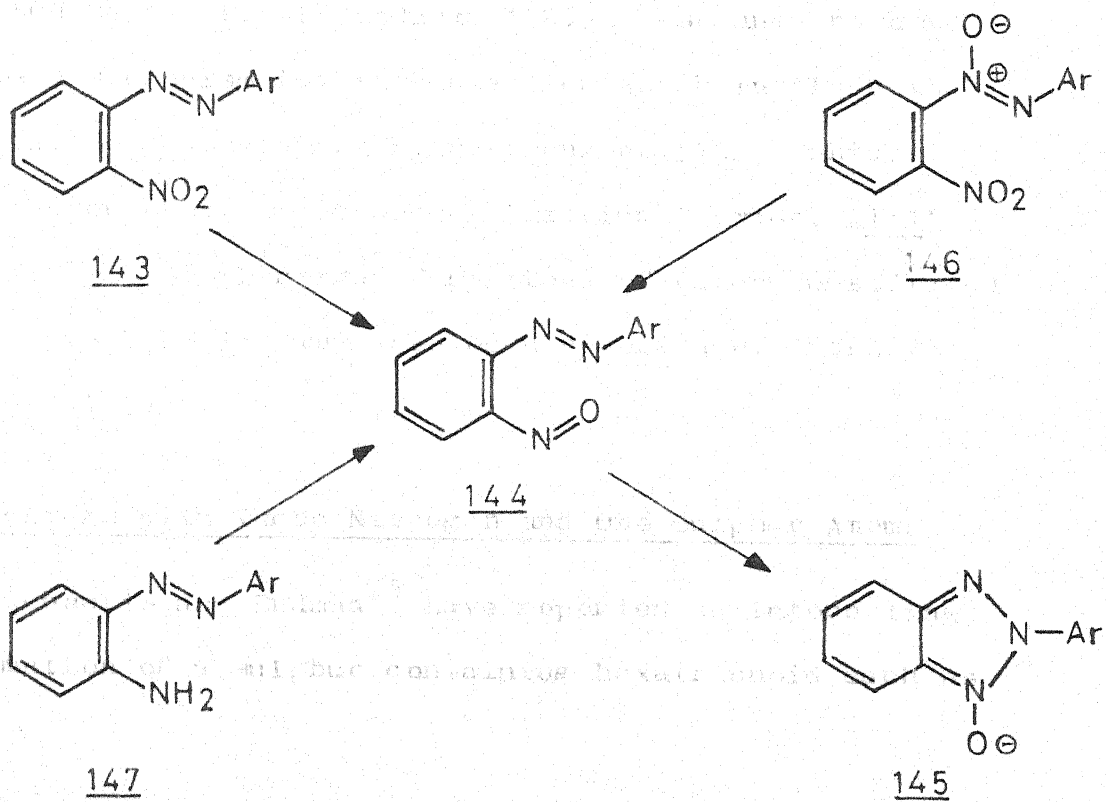
1.5.3 Systems with Three Nitrogen and One Oxygen Atoms

Bamberger had reported the formation of a benzotriazole-1-oxide, 145, in the ammonium sulphide reduction of o-nitro-

Scheme 1.24



Scheme 1.25



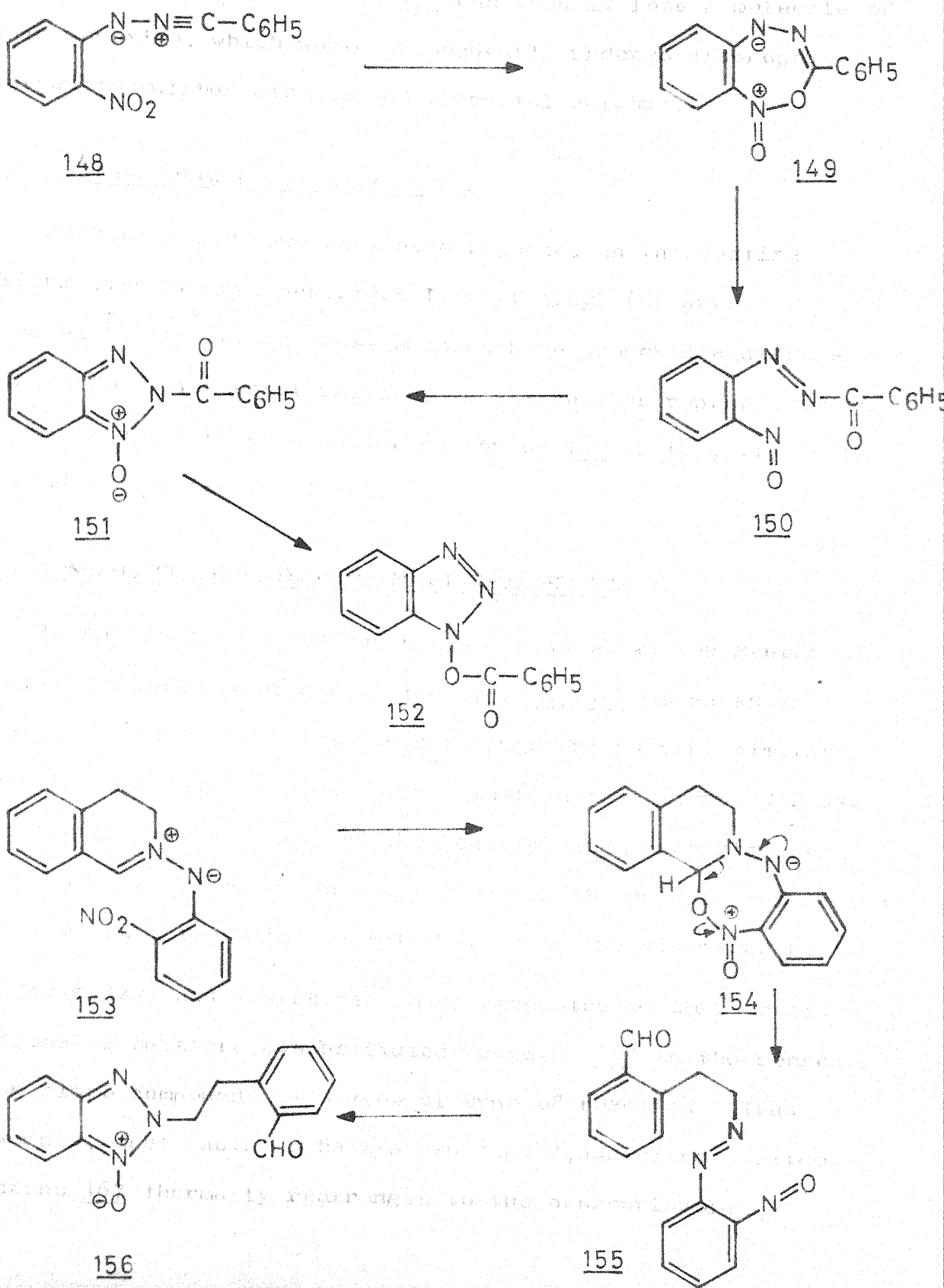
azobenzene (143).⁷⁰ The same benzotriazole-1-oxide is formed both in the reduction of o-nitroazoxybenzene (146)⁷¹ and the oxidation of o-aminoazobenzene (147)⁷² (Scheme 1.25). The formation of 145 in these reactions could result from the valence isomerisation of the intermediate o-nitrosoazobenzene (144).

In section 1.4.2, we have indicated that nitrileimines carrying a o-nitrophenyl substituent on the carbon atom, can exist as the valence isomeric, azoanthranil-N-oxides. Huisgen and coworkers⁷³ have reported a similar interesting transformation in the case of a nitrileimine with a o-nitrophenyl substituent on the nitrogen atom. These authors have shown that a nitrileimine such as 148 undergoes a thermal rearrangement to the benzotriazolium 1-oxide (151), which is subsequently transformed to the final product, 152. These authors have suggested a mechanism for this reaction which involves the intermediacy of o-benzoylazonitrosobenzene (150), which is a valence isomer of 2-benzoylbenzotriazolium 1-oxide, (151) (Scheme 1.26). Similar transformations of other substituted nitrileimines like 153 have also been reported by Grashey⁷⁴ (Scheme 1.26).

1.5.4 Systems with Three Nitrogen and One Sulphur Atoms

Michaelis and Erdman⁷⁵ have reported an interesting transformation of a sulphur containing hexatrienoid such as

Scheme 1.26



157 to the benzotriazole 159 (Scheme 1.27). In this case, the dipolar, triazolium derivative 158 can readily lose a molecule of sulphur monoxide, which would subsequently undergo disproportionation to sulphur dioxide and elemental sulphur.

1.5.5 Systems with Four Oxygen Atoms

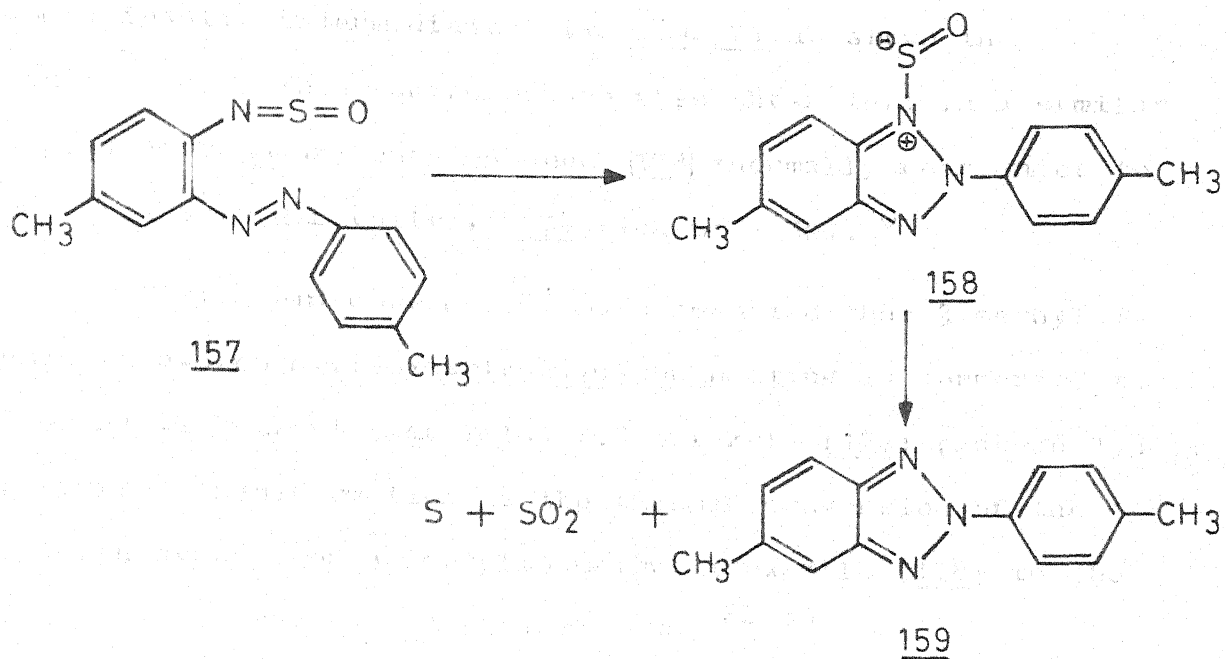
Kashiwagi and coworkers have reported an interesting transformation of acyl peroxides to acyl alkyl (or aryl) carbonates.^{76,77} Though these authors have proposed a different mechanism for this transformation, an alternative representation would involve the valence isomerization of 160 to 161, which can then lead to 162 (Scheme 1.28).

1.6 MONOMOLECULAR HETEROCYCLIC REARRANGEMENTS

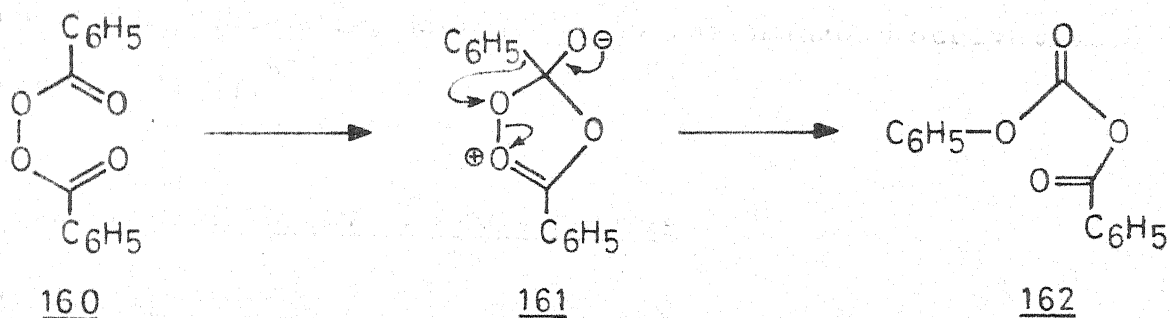
Recently, Ruccia and coworkers⁷⁸ have shown the generality of a class of rearrangements of the type 163-164 as shown in Scheme 1.29. Since this type of rearrangement is very similar to the valence isomerism of 1,3,5-hexatrienoid systems, discussed in the earlier sections of this chapter and these reactions provide an easy method of access to many of the heterohexatrienoid systems, a few interesting examples of these are discussed below.

Katritzky and coworkers⁷⁹ have demonstrated that transformations of suitable o-substituted furoxans 165 to the corresponding nitro compounds is a general type of reaction. Thus for example, these authors have shown that 2,6-dinitro-3-azidoazobenzene 167 thermally rearranges to the benzotriazole

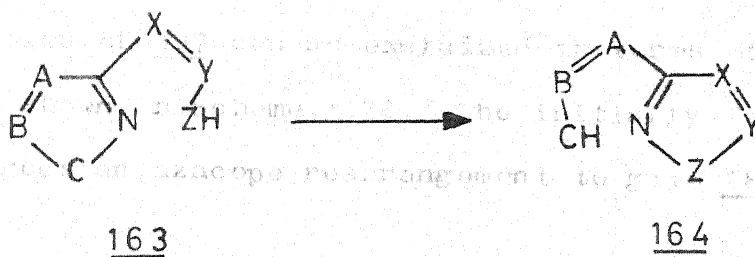
Scheme 1.27



Scheme 1.28



Scheme 1.29



derivative, 172. A probable mechanism for this conversion would involve intermediates like 169-171 as shown in Scheme 1.30. These authors have also shown that in a similar way, o-nitro-m-azidoacetophenone (173) thermally rearranges to the isoxazole derivative, 174 (Scheme 1.30).⁸⁰

Wittig and coworkers⁸¹ have reported that 3-methyl-4-phenylazo-5-phenylisoxazole (176) on heating is converted to 2-phenyl-4-benzoyl-5-methyl-1,2,3-triazole (177) (Scheme 1.31). A similar transformation is the thermal conversion of the phenylhydrazone of 3-acetyl-5-methyl isoxazole (178) to the triazole derivative 179 (Scheme 1.30).^{82,83}

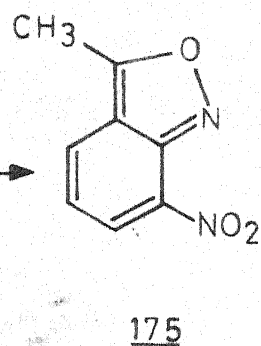
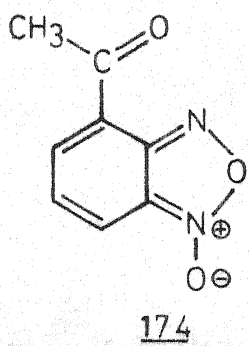
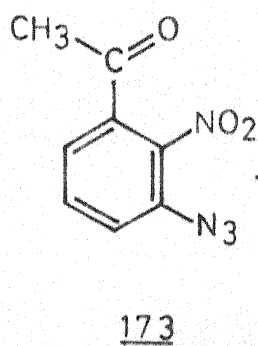
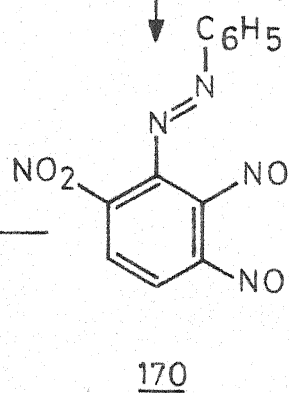
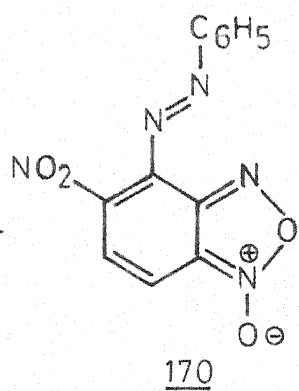
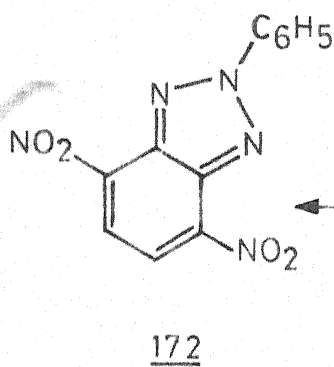
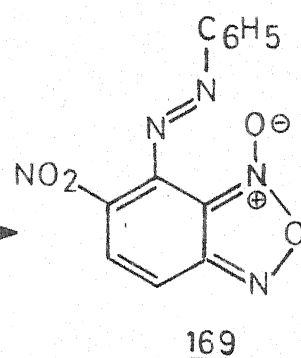
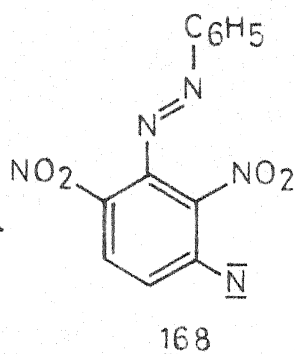
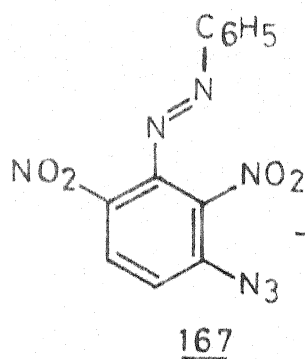
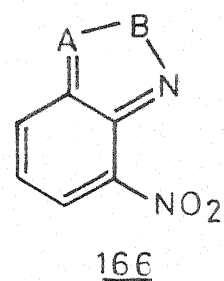
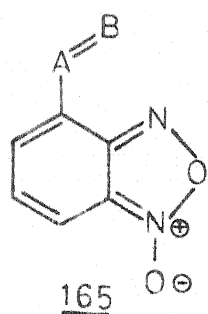
A rearrangement very similar to the transformation of the isoxazole 178 to the triazole, 179 involves the transformation of the 1,2,4-oxadiazole, 180 to the triazole derivative, 181 (Scheme 1.31).^{82,83}

1.7 SYNTHESES INVOLVING VALENCE ISOMERS

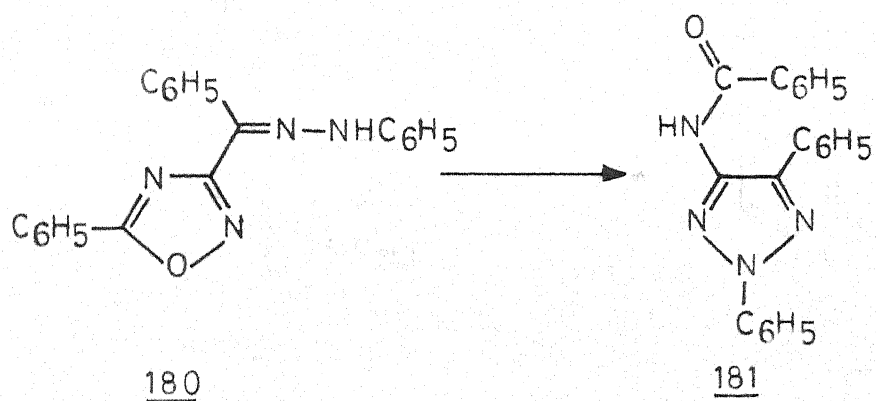
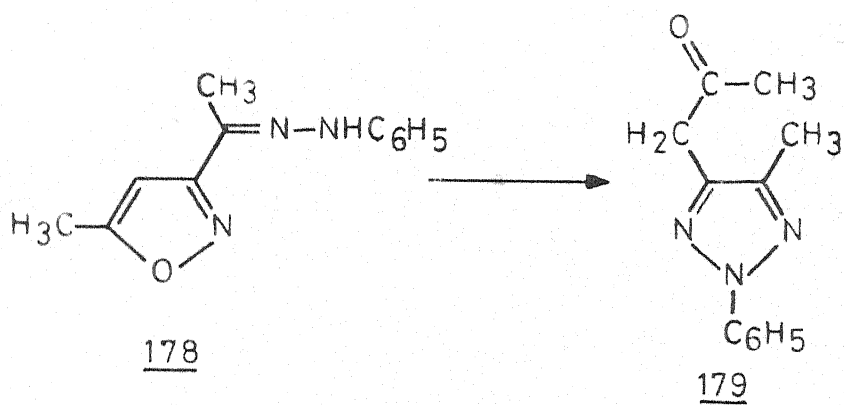
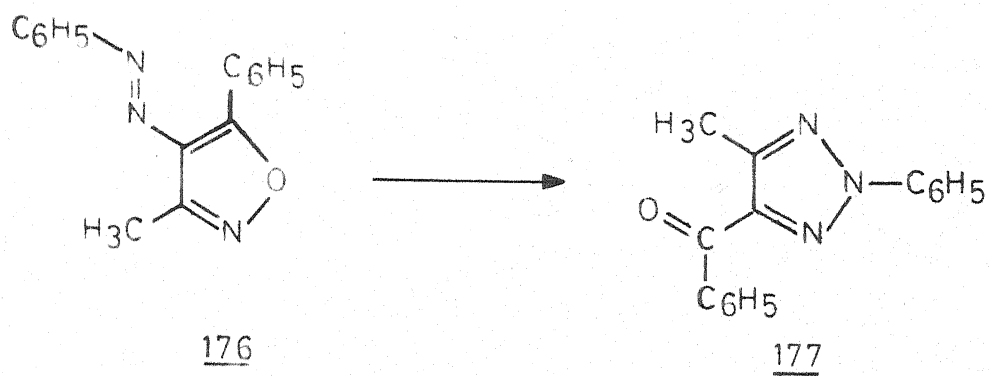
1.7.1 Indole Synthesis

Schiess and Grieder⁸⁴ have reported the formation of the indole derivative, 187 from the reaction of the phenylhydrazine derivative 182 with carbonyl compounds containing an α -methylene group. The formation of 187 can be explained in terms of the reaction sequence shown in Scheme 1.32. The initially formed adduct, 183 undergoes an azacope rearrangement to give 184,

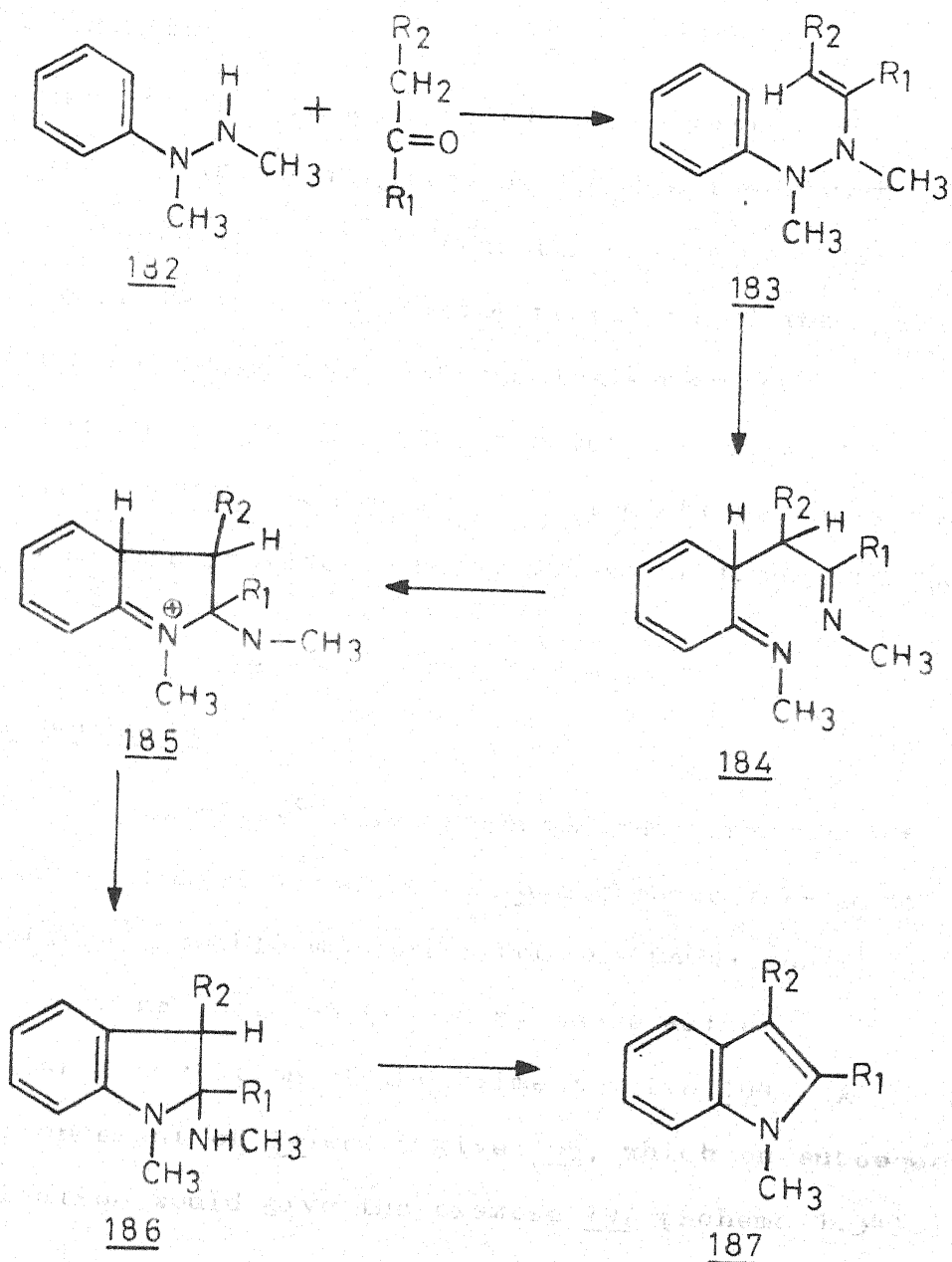
Scheme 1-30



Scheme 1.31



Scheme 1-32



which undergoes valence isomerization to the dipolar intermediate 185. This dipolar intermediate then ultimately gives rise to 187.

1.7.2 Pyrrole Synthesis

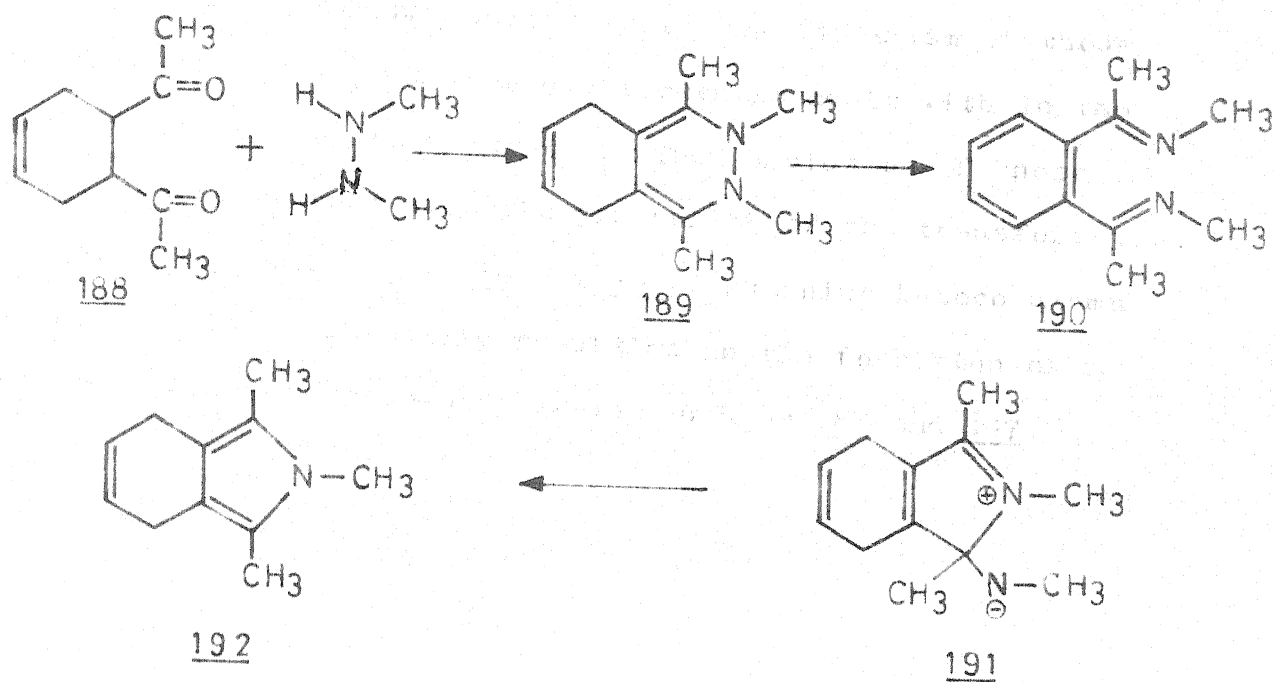
Baldwin and Basson⁸⁵ have reported the formation of 1-substituted pyrroles in the reaction of 1,4-diketones with 1,2-disubstituted hydrazines. This reaction can be mechanistically explained in terms of an initial formation of the 1,2-dihydropyridazine derivative, 189 and its subsequent valence isomerisation to 190 and 191, ultimately leading to the pyrrole derivative 192 (Scheme 1.33). It might be mentioned here that this reaction provides a ready access to 1-substituted pyrroles.

1.7.3 Oxazole Synthesis

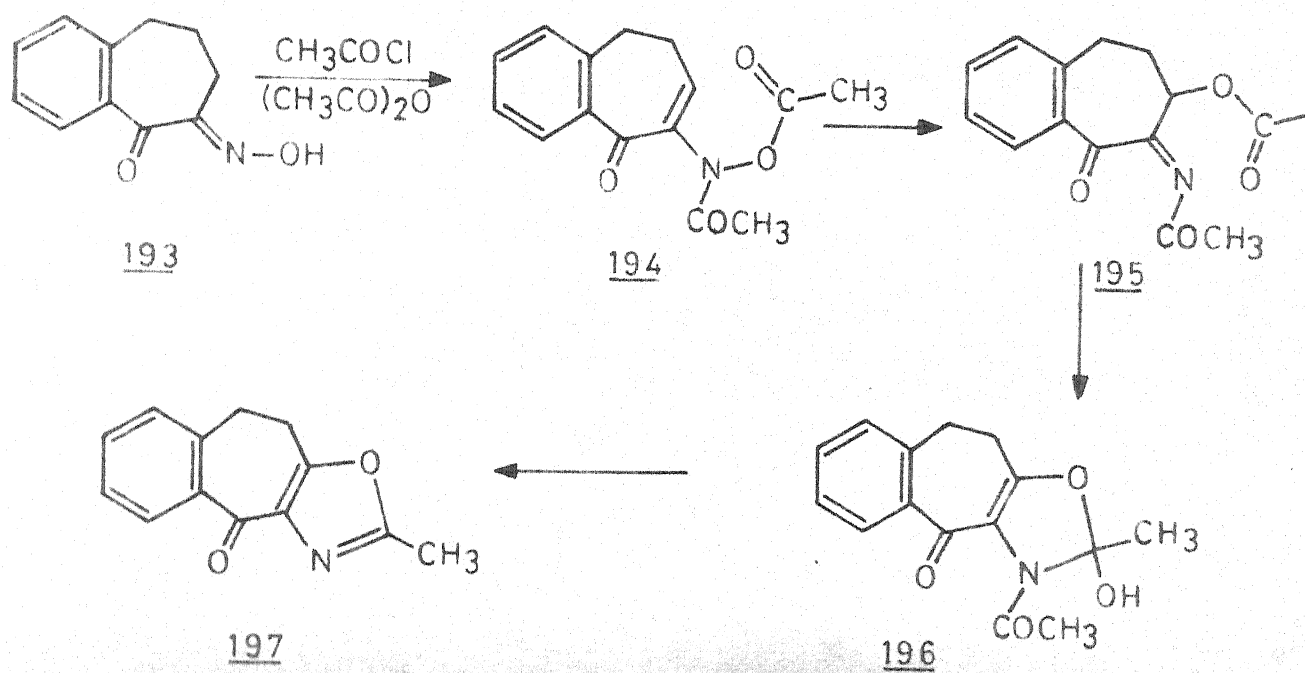
Galantey and coworkers⁸⁶ have reported the formation of oxazoles in the reaction of 1,2-diketone-o-acylmonooximes with acetic anhydride. A probable mechanism for the formation of these products which has been suggested by these authors, involves an initial N-acylation of the oxime to give 194. A heterocope rearrangement of 194 would give 195, which on subsequent valence isomerisation would give the oxazole 197 (Scheme 1.34).

It might be pointed out that the reactions described in sections 1.7.1 and 1.7.3 are not instances of valence

Scheme 1.33



Scheme 1.34



isomerism in hexatrienoids. They are however included here, because of the striking similarity in the mechanism of these reactions to the type of valence isomerism dealt with in the earlier sections of this chapter. The inclusion of these reactions also demonstrates the generality of the transformation of 1,5-hexadienoids like 184 and 195, containing hetero atoms at the termini, ultimately resulting in the formation of a five-membered heteroaromatic system such as 187 and 197.

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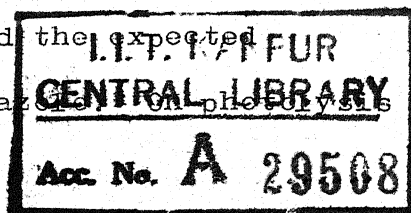
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CHAPTER 2

THERMAL AND PHOTOCHEMICAL TRANS- FORMATIONS OF A FEW BISPHENYLAZOALKENES AND RELATED SYSTEMS¹

2.1 ABSTRACT

The existence of valence tautomeric equilibrium between 1,2-bisphenylazoalkenes and anhydro 1-phenylimino-2-phenyl-4,5-disubstituted-1,2,3-triazolium hydroxides has been demonstrated by their thermal and photochemical fragmentation behaviours. Thus, 1,2-bisphenylazostilbene when photolysed in benzene gave 2,4,5-triphenyl-1,2,3-triazole. The same triazole was formed when 1,2-bisphenylazostilbene was heated to its melting point. Similarly, 1,2,3-triazoles were obtained both in the thermolysis and photolysis of 1,2-bisphenylazodi(4-chlorophenyl)ethylene and 1,2-bisphenylazodi(4-methoxyphenyl)ethylene. Thermolysis of 1,2-bisphenylazocyclohexene yielded the expected 1,2-phenyl-4,5-tetramethylene-1,2,3-triazole. On photolysis of



1,2-bisphenylazocyclohexene, a mixture of 2-phenyl-4,5-tetramethylene-1,2,3-triazole and 1-anilino-2-phenyl-1,4,5,6-tetrahydrocyclohexa[d]-1,2,3-triazole were obtained. Both 2,3-bisphenylazo-2-butene and 1,2-bisphenylazoethylene failed to undergo either thermolysis or photolysis, under similar conditions. However, when photolysed in presence of hydrochloric acid, bisphenylazo-2-butene gave 2-phenyl-4,5-dimethyl-1,2,3-triazole. The formation of triazoles in the above mentioned reactions has been explained in terms of the valence isomers of these bisphenylazoalkenes, namely, anhydro-1-phenylimino-2-phenyl-4,5-disubstituted-1,2,3-triazolium hydroxides. o-Phenylazophenyldiazocyanide under both photochemical and thermal conditions gave the expected 2-phenyl-4,5-benzo-1,2,3-triazole. An azomethineimine such as, C-biphenylene- N^{α} -(4-chlorophenyl)- N^{β} -cyanoazomethineimine gave 9-fluorenone(4-chlorophenyl) anil, both under thermal and photolytic conditions. 1,2-Bisphenylazoacenaphthylene failed to undergo photolysis and thermolysis under similar experimental conditions. However, when it was irradiated in methanol, acenaphthenequinone monophenylhydrazone was obtained.

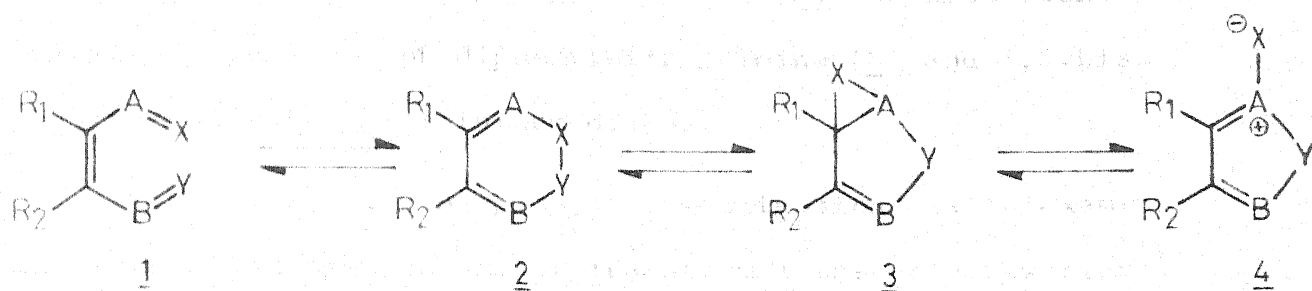
2.2 RESULTS AND DISCUSSION

In Chapter 1 we have cited several examples of valence isomerisation of 1,3,5-hexatriene systems containing heteroatoms like nitrogen, oxygen and sulphur. Also, it has been

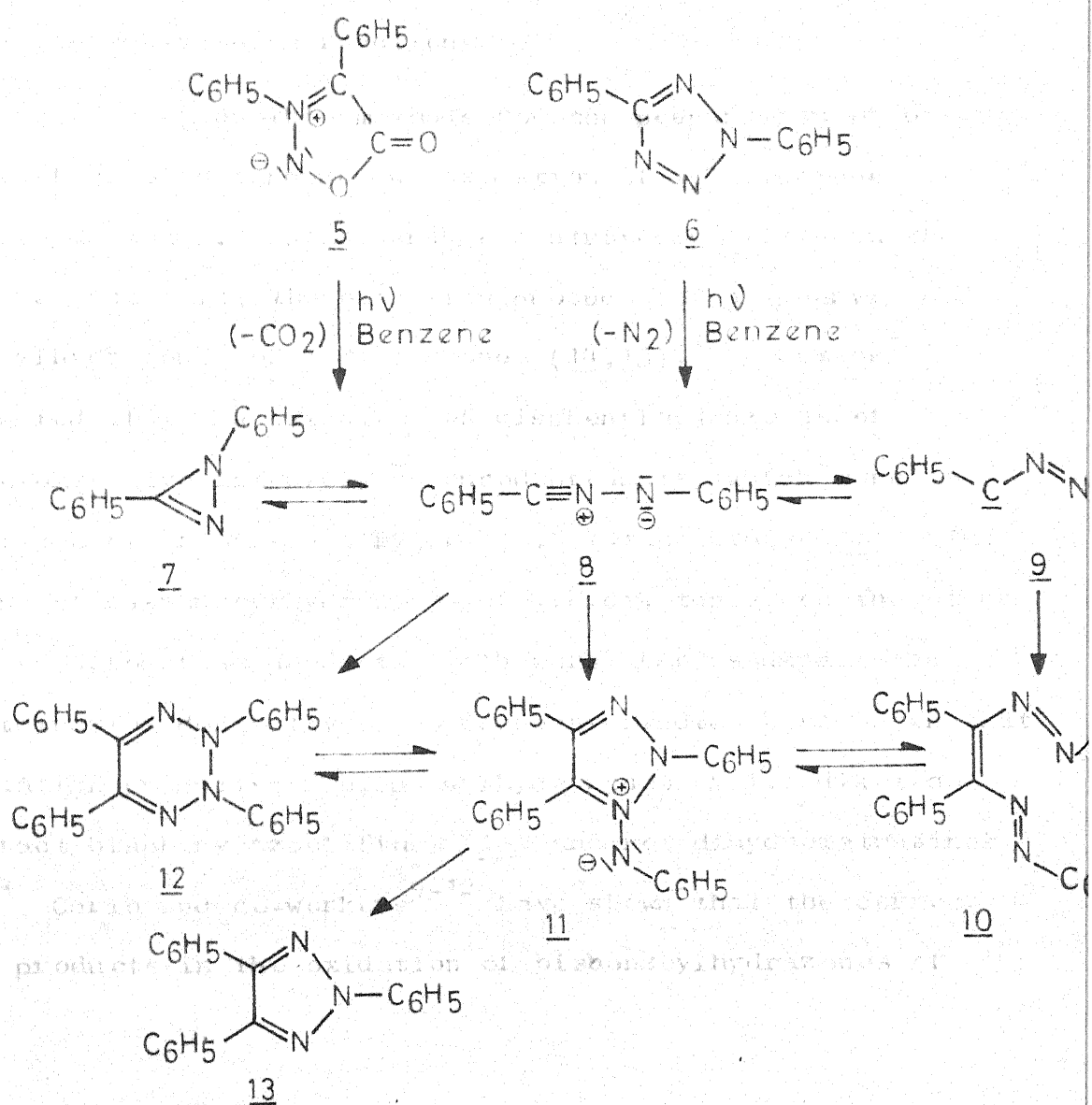
pointed out that several interesting transformations of these systems can be rationalized in terms of their valence isomers, which in turn will undergo further transformations depending on the nature of the starting hetero systems. A trienoid system like (1), for example, is capable of undergoing valence isomerisation and structures like (2), (3) and (4) could represent some of the possible isomers (Scheme 2.1).

In a detailed investigation on the photochemical transformation of sydnones and related systems, Angadiyavar and George² have shown that 1,2-bisphenylazostilbenes could be involved as intermediates in these reactions. Thus, for example, the formation of 2,4,5-triphenyl-1,2,3-triazole in the photolysis of N,C-diphenylsydnone (5) has been rationalised in terms of the intermediacy of 1,2-bisphenylazostilbene (10). It has been suggested that N,C-diphenylsydnone undergoes an initial photochemical fragmentation to diphenylnitrileimine (8) which subsequently dimerises to the bisazoalkene (10). The bisazoalkene (10) can then undergo a valence isomerization to anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide (11), which in turn can lose phenylnitrene leading to the triazole (13). The anhydro iminotriazolium hydroxide (11) could also be formed directly through a 1,3-dipolar cycloaddition of diphenylnitrileimine (8) with another nitrileimine moiety (Scheme 2.2). Similarly, the formation of the triazole (13) in the photochemical

Scheme 2.1



Scheme 2.2



transformation of 2,5-diphenyltetrazole (6) has also been explained in terms of diphenylnitrileimine (8) and 1,2-bis-phenylazostilbene (10) intermediates.

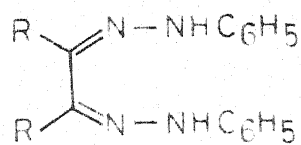
The object of the present investigation was to examine the thermal and photochemical transformations of a few representative examples of bisazoalkenes to see whether they undergo valence isomerisation to the corresponding imino-triazolium derivatives and also to examine the nature of products formed in these reactions.

One of the possible methods for the preparation of bis-phenylazoalkenes is through the oxidation of 1,2-diketone bisphenylhydrazones.³ Considerable controversy exists in the literature concerning the oxidation products of bisphenyl and bisbenzoylhydrazones of 1,2-diketones (14,15).⁴ Pechmann⁵ had reported that the oxidation of bisphenylhydrazones of 1,2-diketones give intensely coloured products, which were designated earlier as 2,3-dihydro-1,2,3,4-tetrazines (12). The oxidation of bisbenzoylhydrazones of 1,2-diketones, on the other hand, gave colourless products which were also assumed to be dihydrotetrazine derivatives. Subsequent studies have shown that the oxidation products of bisphenylhydrazones of 1,2-diketones are in fact bisphenylazoclefines (10) and not dihydrotetrazines (12).⁶⁻⁸ Curin^k and co-workers⁹⁻¹² have shown that the corresponding products in the oxidation of bisbenzoylhydrazones of

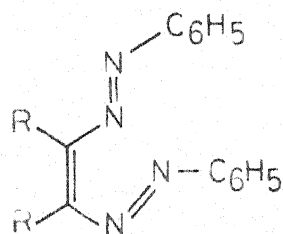
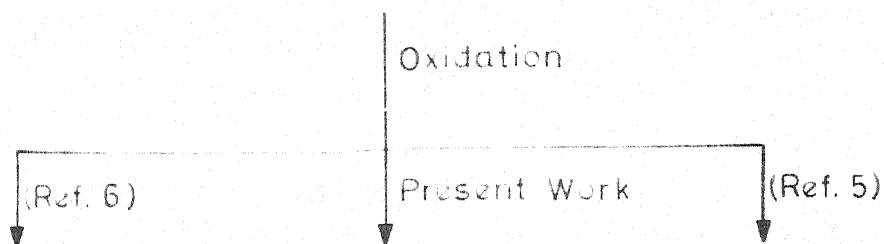
1,2-diketones are correctly represented as enol benzoates and that these enol benzoates (17) undergo ready rearrangement to dibenzoyl derivatives of N-aminotriazoles (18), presumably, through a four-membered cyclic transition state. Quite recently, Petersen and Heitzer¹³ have, on the basis of high resolution nmr studies, shown that the product obtained from the oxidation of biacetyl bisbenzoylhydrazone exists as the mesoionic anhydro 1-benzoylimino-2-benzoyl-4,5-dimethyl-1,2,3-triazolium hydroxide (16). Katritzky and coworkers¹⁴ have questioned the assignment of such mesoionic structures to the oxidation products of bisbenzoylhydrazones. These authors, however, concede that such mesoionic structures may be probable in the case of orthobisazo compounds in which one of the azo groups is electrophilically substituted.¹⁵ Thus, it has been pointed out that a bisazoalkene such as *o*-phenylazophenyldiazocyanide (19) could exist in the mesoionic form (20) (Scheme 2.3).

It has been possible for us to show that bisphenylazoalkenes (10) are capable of undergoing 1,3-dipolar cycloaddition reactions with different dipolarophiles (see, Chapter 3).^{16,17} These reactions are best explained in terms of the phenylimino-triazolium hydroxide structures (11), which are essentially valence isomers of the starting bisazoalkenes (10). It is pertinent to observe here that all the three structures (10), (11) and (12), which have been suggested for the oxidation

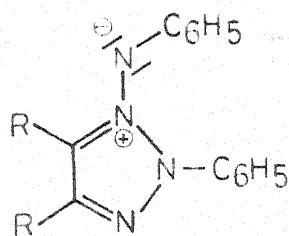
Scheme 2.3



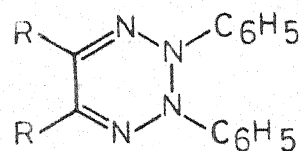
- 14) a, $\text{R}=\text{C}_6\text{H}_5$
 b, $\text{R}=\text{2-Cl-C}_6\text{H}_4$
 c, $\text{R}=\text{2-CH}_3\text{O-C}_6\text{H}_4$



10 a-c

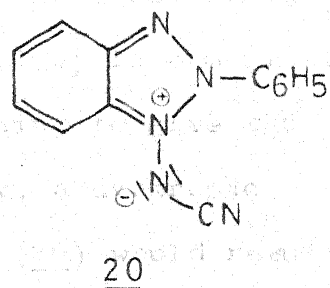
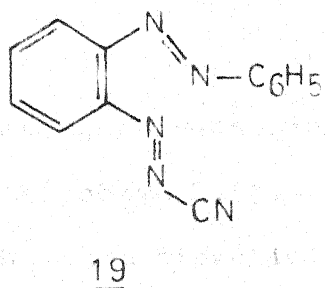
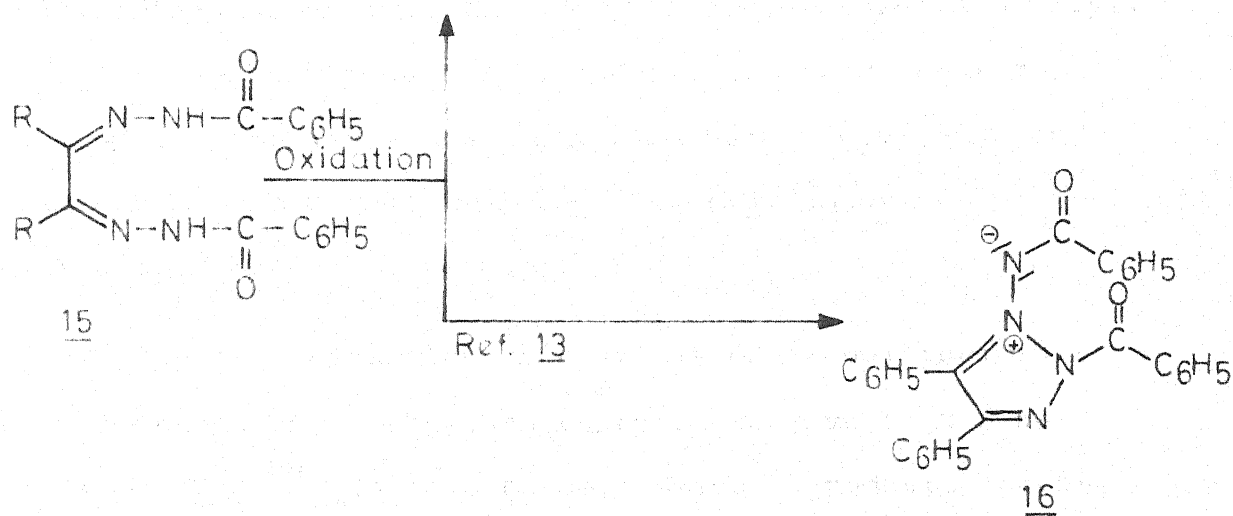
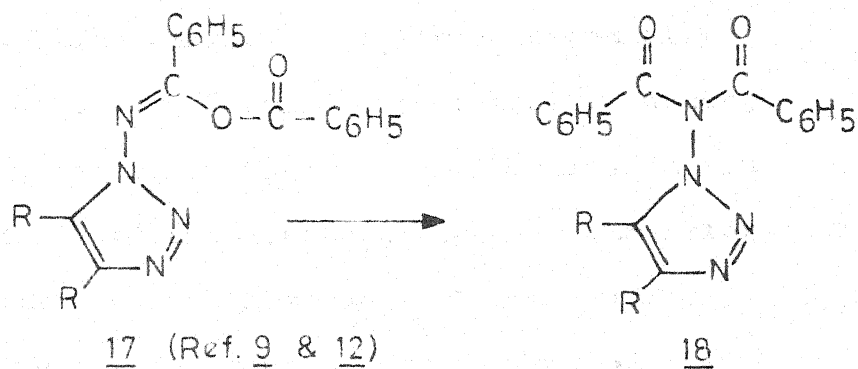


11 a-c



12 a-c

Scheme 2.3 (Contd.)

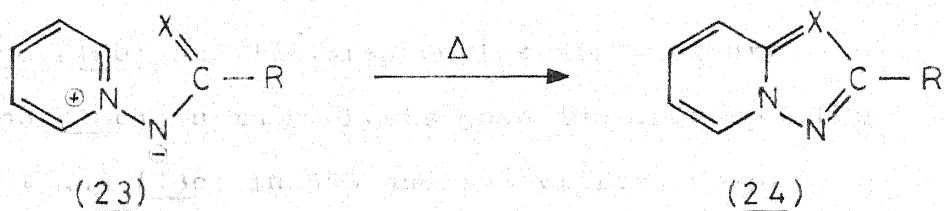
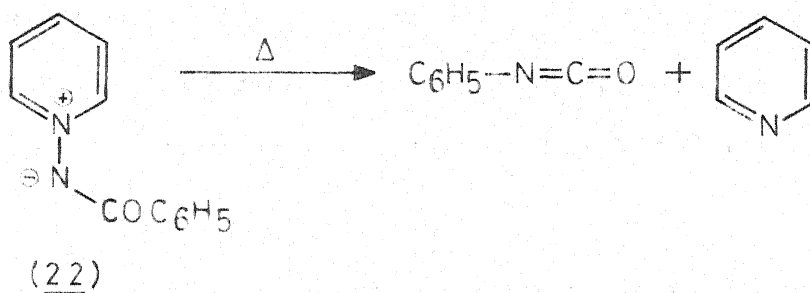
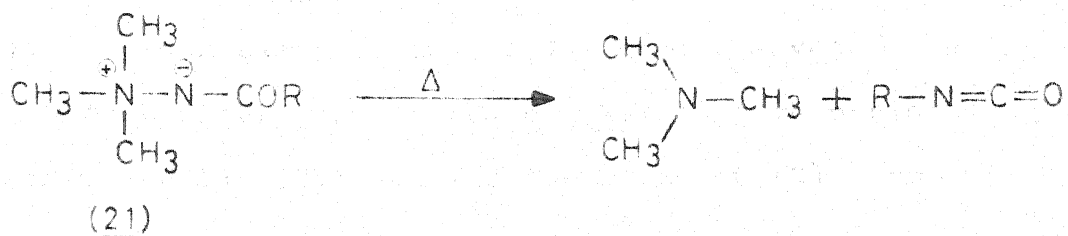


products of bisphenylhydrazones of 1,2-diketones are valence isomeric forms of the same compound.

The iminotriazolium hydroxides (11) are essentially azomethineimines and as such one would expect them to undergo reactions typical of azomethineimines. Azomethineimines, in general, are reported to undergo different types of transformations, both under thermal and photochemical conditions, depending on their structural features. Thus, for example, trimethylamine-N-acylimine such as (21) and pyridine-1-benzoylimine (22) have been reported to undergo N-N bond cleavage, on heating to give the parent amines (Scheme 2.4).¹⁸⁻²⁰ On the other hand, an azomethineimine like (23) undergoes a thermal cyclisation to give (24).²¹⁻²³

The photochemical transformations of azomethineimines like pyridine-N-imines (25) are reported to give diazepine derivatives (27).²⁴ In some cases, however, products corresponding to amination at the ortho-position have also been observed.²⁴⁻²⁶ The formation of diazepines in these reactions has been explained in terms of a bicyclo[4,1,0] intermediate (26), which undergoes subsequent ring opening to give the diazepine (27) (Scheme 2.5). Alternatively, a dyotropic reaction of the same bicyclic intermediate (26) would result

Scheme 2.4

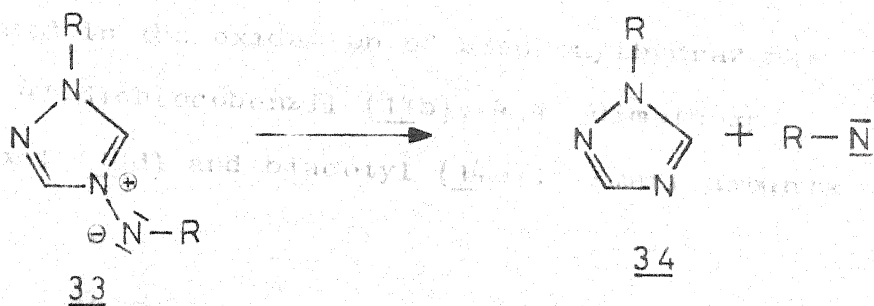
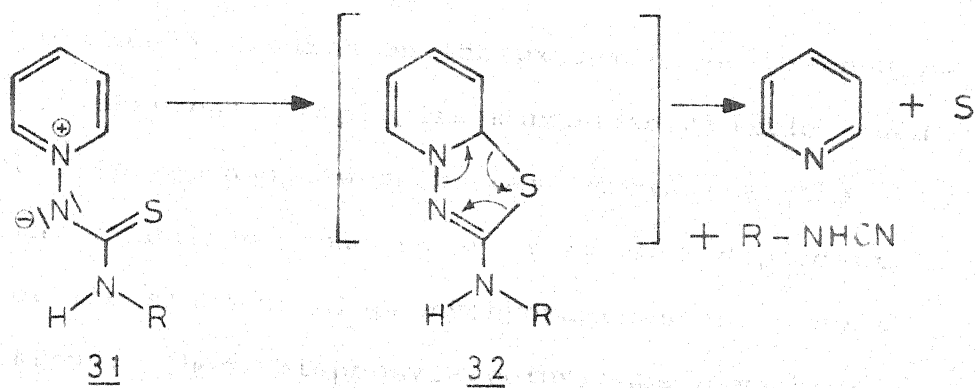
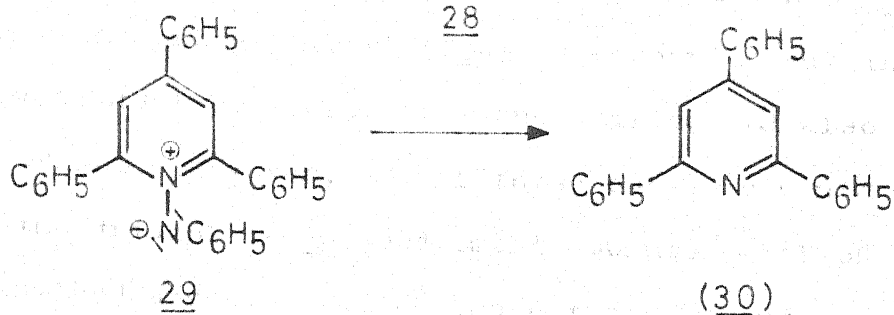
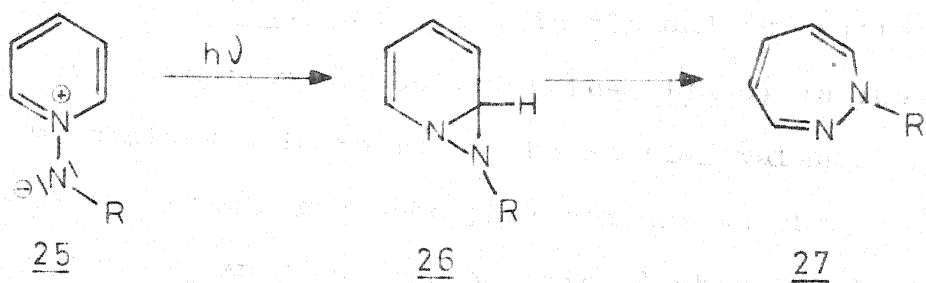


in the ortho-aminated product (28).²⁷ Products corresponding to N-N bond cleavage have also been reported in the photolysis of pyridine-N-imines.^{24,26} Thus, for example, 1-phenylimino-2,4,6-triphenylpyridine (29), on photolysis gives rise to 2,4,6-triphenylpyridine (30) with the loss of phenylnitrene (Scheme 2.5).²⁵ Other examples of the N-N bond cleavage involve the photochemical deamination of (31) to give pyridine, through the intermediate (32) and the formation of (34) from (33).²⁶

With a view to establishing whether the intermediate involved in the photolysis of N,C-diphenylsydnone is 1,2-bisphenylazostilbene (10), we have examined the thermal and photochemical transformations of 1,2-bisphenylazostilbene and also of other representative bisphenylazobenzenes.

Direct heating of bisphenylazostilbene (10) around 175-180° gave a 85% yield of 2,4,5-triphenyl-1,2,3-triazole (13a). The same triazole (13a) was obtained in a 71% yield when a solution of (10a) was irradiated in benzene solution for 30 minutes. Similarly, 1,2-bisphenylazodi(4-chlorophenyl)ethylene (10b) and 1,2-bisphenylazodi(4-methoxyphenyl)ethylene (10c) on thermolysis gave the corresponding triazoles (13b) and (13c) in 55% and 89% yields, respectively. On the other hand, irradiation of benzene solutions

Scheme 2.5

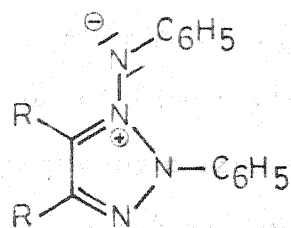
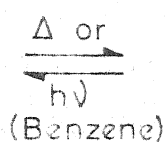
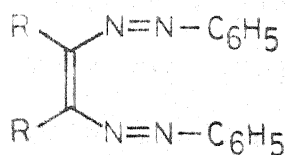


of (10b) and (10c) gave (13b) and (13c) in 55% and 60% yields, respectively. The formation of the triazoles (13a-c) in these reactions can be explained in terms of the initial valence isomerisation of the starting bisphenylazoalkenes to the corresponding mesoionic anhydro 1-phenylimino-2-phenyl-4,5-diaryl-1,2,3-triazolium hydroxides (11a-c) and subsequent loss of phenylnitrene to give the products (13a-c) (Scheme 2.6).

In a possible attempt to trap the phenylnitrene formed in the thermolysis and photolysis of bisphenylazoalkenes (10a-c), the thermolysis and photolysis of (10a) were carried out in presence of solvents like cyclohexene and aniline and also cycloocta-1,3-diene. However, in all these cases we could isolate only the triazole (13a) and small amounts (~5%) of benzil bisphenylhydrazone. None of the nitrene insertion products could be obtained from these runs (Scheme 2.6).

In their extensive studies on the oxidation of bisphenylhydrazones of 1,2-diketones, employing manganese dioxide²⁸ and nickel peroxide,³ George and coworkers have shown that the structures of the oxidation products are very much dependant on the nature of the starting bisphenylhydrazones and also the reaction conditions. Thus, bisphenylazoethylenes have been reported to be formed in the oxidation of bisphenylhydrazones of benzil (14a), 4,4'-dichlorobenzil (14b), 4,4'-dimethoxybenzil (14c), glyoxal (14d) and biacetyl (14e). Small amounts

Scheme 2.6

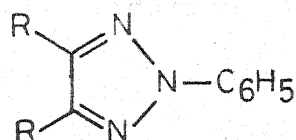


10 a, R=C₆H₅

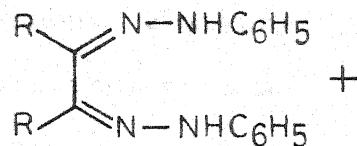
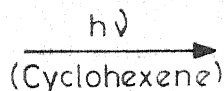
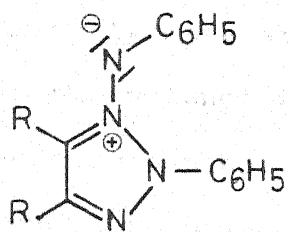
b, R=p-Cl-C₆H₄

c, R=p-CH₃O-C₆H₄

11 a-c



13 a-c

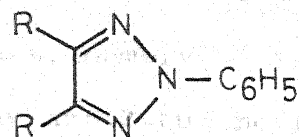


11 a, R=C₆H₅

b, R=p-Cl-C₆H₄

c, R=p-CH₃O-C₆H₄

14 a-c

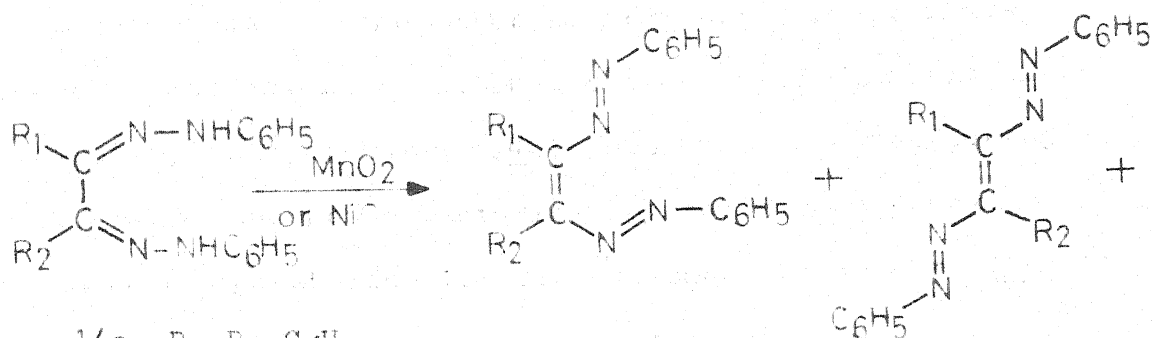


13 a-c

of triazoles (13a-c) have also been formed as side products in the oxidation of (14a-c). In the oxidation of biacetyl bisphenylhydrazones (14e), methylglyoxal bisphenylhydrazones (14f) and methylphenylglyoxal bisphenylhydrazones (14g), the formation of phenylazopyrazoles (35a-c) has also been observed. The oxidation of phenylglyoxal bisphenylhydrazones (36), on the other hand, gave a mixture of products consisting of 2,3,5,6-tetraphenyl-1,2,4,5-tetraazapentalene (37) and 2,4-diphenyl-1,2,3-triazole (38) (Scheme 2.7).³

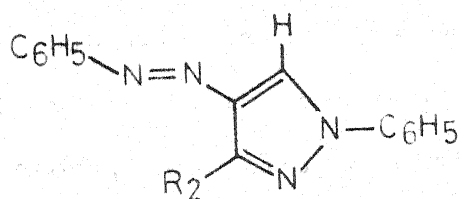
The bisphenylazoalkenes formed from the oxidation of bisphenylhydrazones of 1,2-diketones can have either a cis or trans geometry around the carbon-carbon double bond. So far, no attempt has been made in assigning the stereochemistry of these bisazoalkenes. It is, however, reasonable to assume that in the absence of overriding steric constraints, the bisphenylazoalkenes will exist in the trans form which is thermodynamically more stable. It is also reasonable to assume that the valence isomerisation of bisphenylazoalkenes will be more pronounced in the case of the cis-isomers than the trans ones, if other factors are not involved. With a view to testing the validity of these assumptions, we have examined the thermal and photochemical transformations of two representative examples of bisphenylazoalkenes, namely, bisphenylazocyclohexene (40) and 2,3-bisphenylazo-2-butanone (10e).

Scheme 2-7

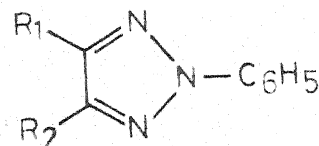


- 14a, $\text{R}_1=\text{R}_2=\text{C}_6\text{H}_5$
b, $\text{R}_1=\text{R}_2=\text{p-Cl-C}_6\text{H}_4$
c, $\text{R}_1=\text{R}_2=\text{p-CH}_3\text{O-C}_6\text{H}_4$
d, $\text{R}_1=\text{R}_2=\text{H}$
e, $\text{R}_1=\text{R}_2=\text{CH}_3$
f, $\text{R}_1=\text{CH}_3$, $\text{R}_2=\text{H}$
g, $\text{R}_1=\text{C}_6\text{H}_5$, $\text{R}_2=\text{CH}_3$

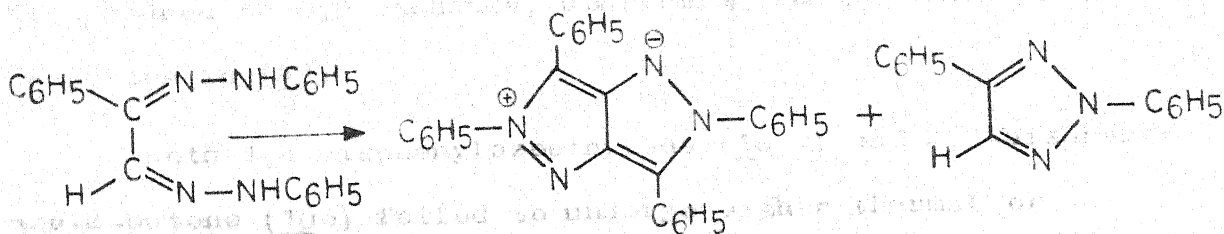
- 10a, $\text{R}_1=\text{R}_2=\text{C}_6\text{H}_5$
b, $\text{R}_1=\text{R}_2=\text{p-Cl-C}_6\text{H}_4$
c, $\text{R}_1=\text{R}_2=\text{p-CH}_3\text{O-C}_6\text{H}_4$
10 d, $\text{R}_1=\text{R}_2=\text{H}$
e, $\text{R}_1=\text{R}_2=\text{CH}_3$



- 35 a, $\text{R}=\text{CH}_3$
b, $\text{R}=\text{H}$
c, $\text{R}=\text{C}_6\text{H}_5$



- 13 a, $\text{R}_1=\text{R}_2=\text{C}_6\text{H}_5$
b, $\text{R}_1=\text{R}_2=\text{p-Cl-C}_6\text{H}_4$
c, $\text{R}_1=\text{R}_2=\text{p-CH}_3\text{O-C}_6\text{H}_4$



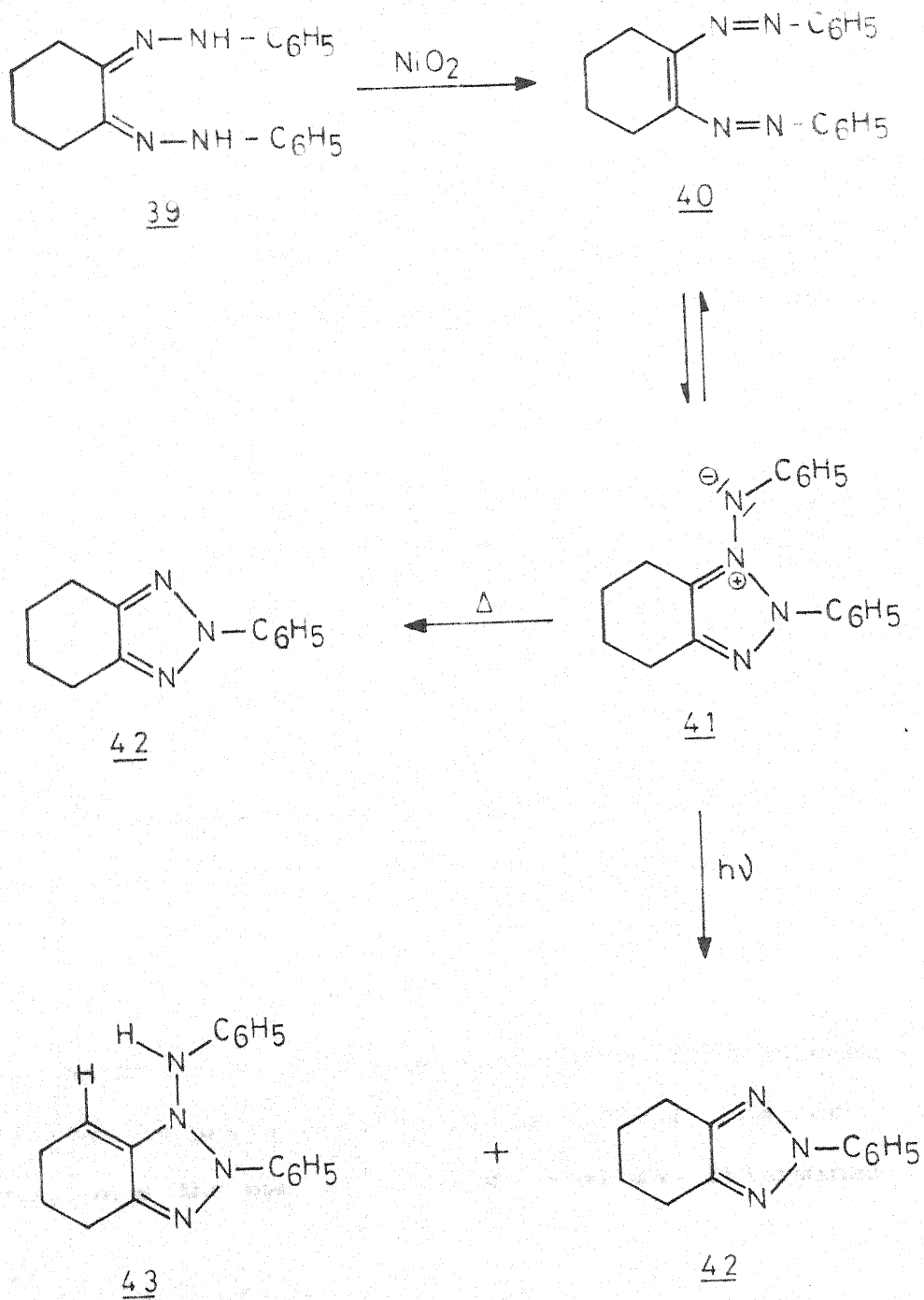
36

37

Of these two bisphenylazoalkenes, (40) will have a cis-configuration due to the built-in structural constraints, whereas, (10e) may have either a cis or trans-configuration. 1,2-Bisphenylazocyclohexene (40), has been prepared during the course of the present studies, by the nickel peroxide oxidation of cyclohexene-1,2-dione bisphenylhydrazone (39) in a 82% yield. Direct heating of (40) around 140° for 20 minutes gave a 14% yield of a product, identified as 2-phenyl-4,5-tetramethylene-1,2,3-triazole (42). The photolysis of (40) in benzene solution, however, gave a 28% yield of the triazole (42) (Scheme 2.8). In addition, a 5% yield of a product melting at 136° and isomeric with (40) was obtained which has been identified as 1-anilino-2-phenyl-1,4,5,6-tetrahydrocyclohexa-[d] 1,2,3-triazole (43), on the basis of analytical results and spectral data. The nmr spectrum of (43) showed a broad multiplet in the range of 7.0-8.0 δ (10 H) due to phenyl protons, and complex multiplets centered around 2.15 δ (4 H) and 2.95 δ (2 H), respectively, due to the methylene protons. In addition, the spectrum showed a multiplet around 4.35 δ (1 H) due to the vinylic proton and a broad singlet around 3.75 δ (1 H) due to the NH proton. The signal at 3.75 δ disappeared on D₂O exchange, confirming the presence of the NH proton in (43).

Both 1,2-bisphenylazoethylene (10 d) and 2,3-bisphenyl-azo-2-butene (10e) failed to undergo either thermal or

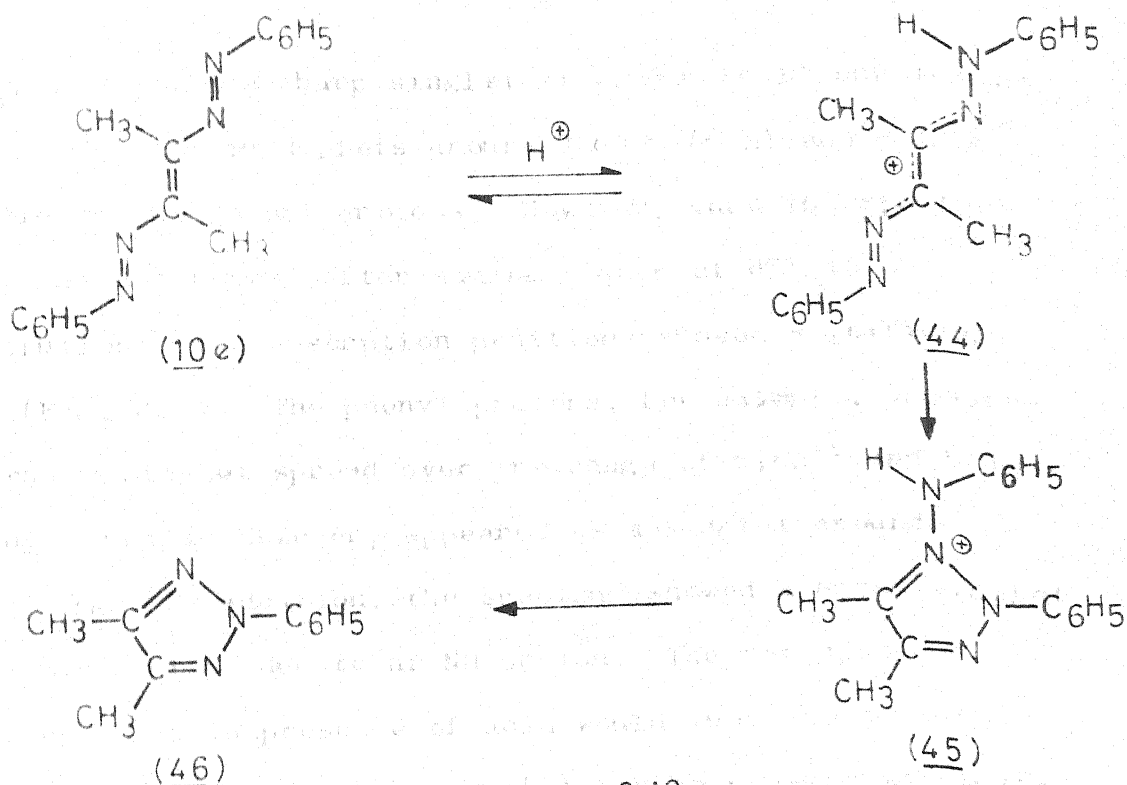
Scheme 2.8



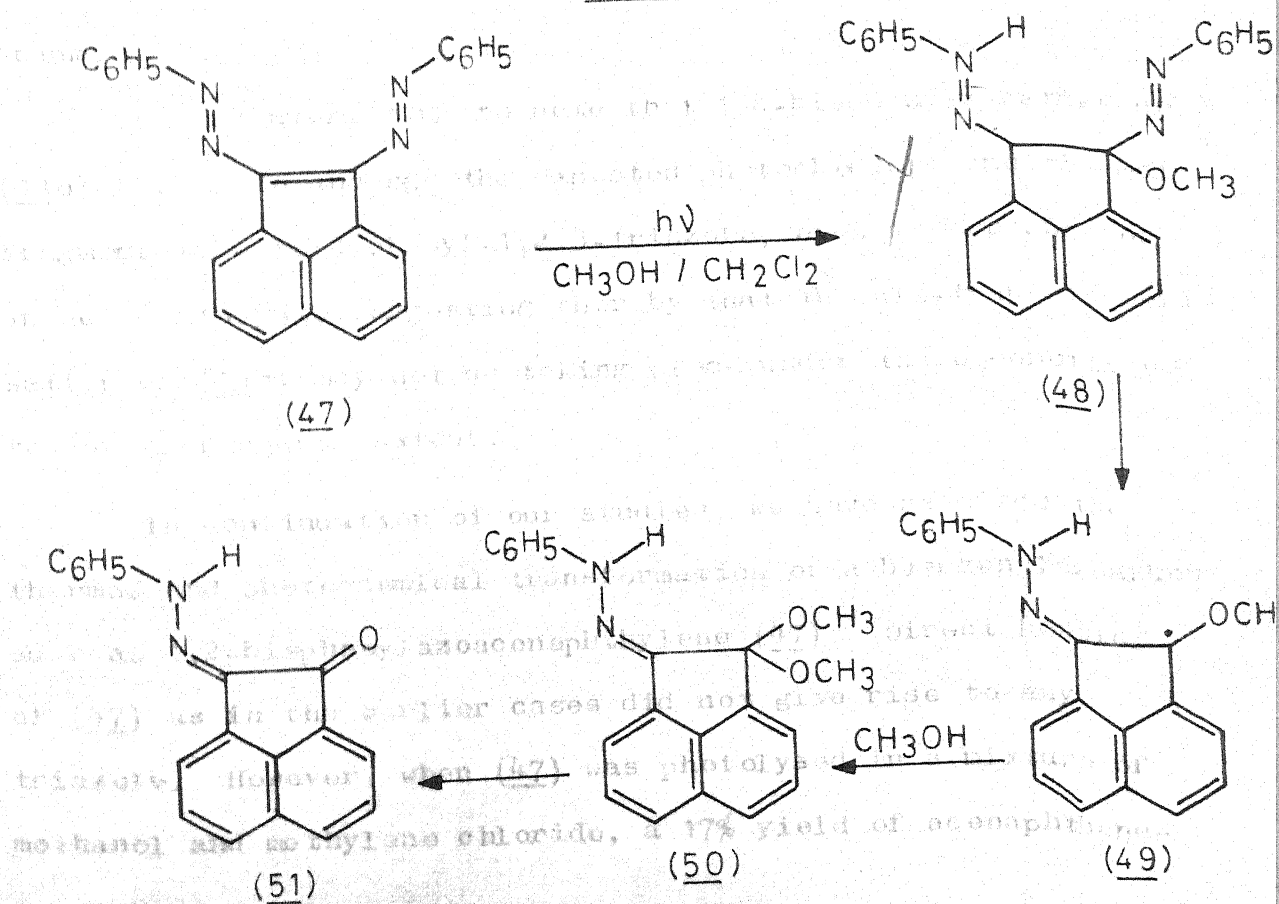
photochemical transformation to give the expected triazoles. The inertness of these bisphenylazoalkenes can be understood if we assume that they have the trans geometry and that the cis-trans isomerisation may not be very facile, under the reaction conditions. It might be mentioned in this connection that 2,3-bisphenylazo-2-butene (10e) is reported to undergo an acid-catalysed transformation to 2-phenyl-4,5-dimethyl-1,2,3-triazole (46).⁵ It would be reasonable to assume that in presence of the acid catalyst, (10e) undergoes a cis-trans isomerisation through the protonated species (44), and finally is converted to the triazole (42), through the cyclic intermediate (45) (Scheme 2.9).

During the course of the present investigation, we have attempted the photolysis of a bisphenylazoalkene such as (10e), in presence of dry HCl, with a view to ascertaining whether the triazole (46) will be formed under these conditions. Irradiation of a benzene solution of 10e, through which dry HCl gas was bubbled, for 5 minutes resulted in the formation of a 55% yield of the triazole (46). The formation of (46) in good yields under these conditions would strongly support the mechanistic pathway outlined in Scheme 2.9.

Further evidence for the isomerisation of 2,3-bisphenylazo-2-butene (10e) in presence of acid was derived from nmr studies. Thus, when the nmr spectrum of (10e) was determined



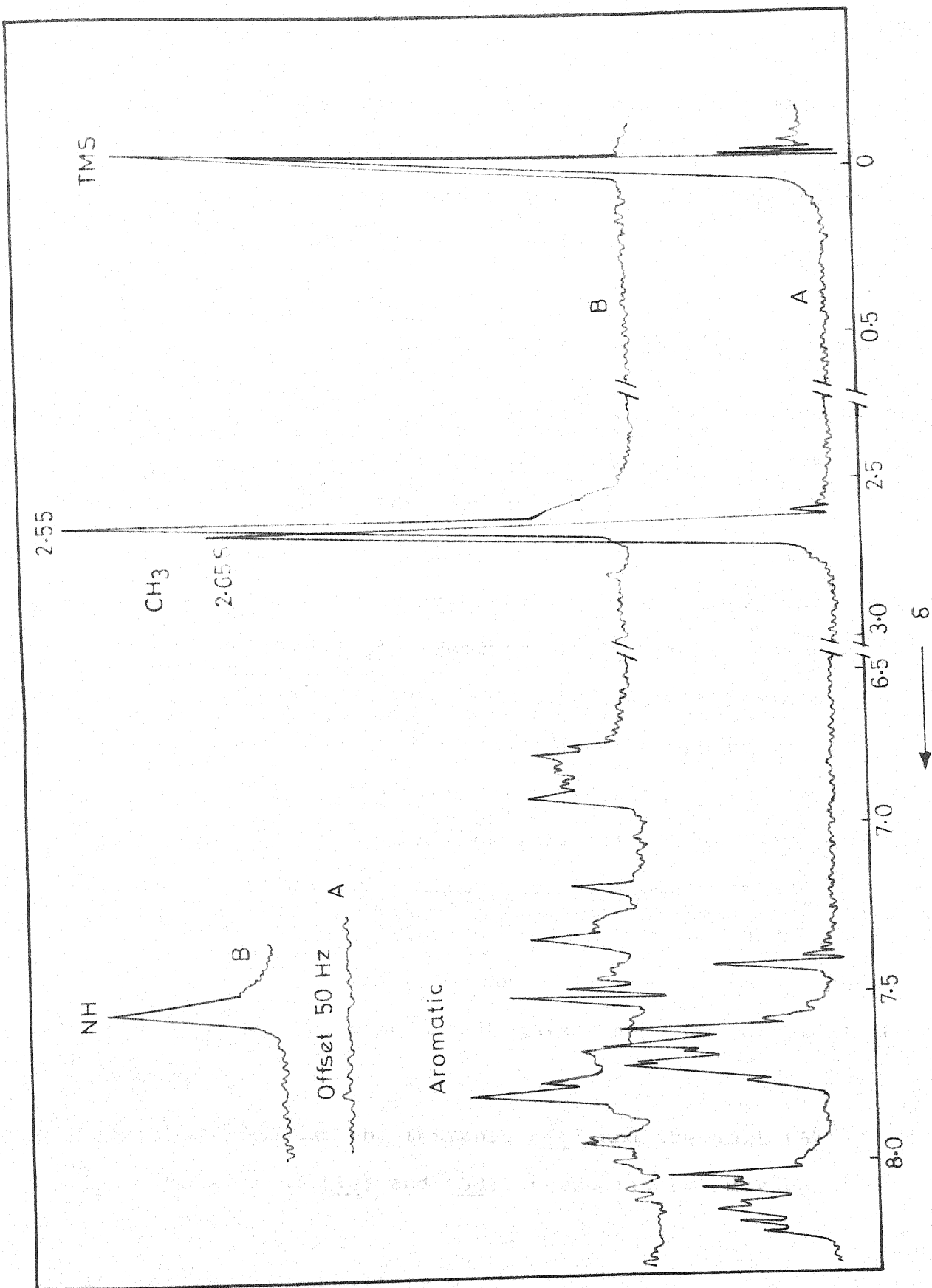
Scheme 2.10



in CDCl_3 , it showed a sharp singlet at 2.65 δ (6 H) due to the methyl protons and multiplets around 7.60 δ (6 H) and 8.10 δ (4 H), due to the phenyl protons. However, when the spectrum of (10e) was determined after adding a drop of HCl to the CDCl_3 solutions, the absorption positions showed significant changes (Fig. 2.1). The phenyl protons, for example, appeared as a broad multiplet spread over the range of 6.80 δ and 8.10 δ . The methyl groups, however, appeared as a singlet around 2.55 δ (6 H). In addition, the spectrum showed a broad singlet around 8.70 δ (1 H) due to an NH proton. The nmr spectral details of (10e) in presence of acid would indicate that the protonated species like (44) and (45) may be present in equilibrium.

It is interesting to note that 1,2-bisphenylazoethylene (11d) failed to undergo the expected photochemical and thermal fragmentation to 2-phenyl-1,2,3-triazole, even in presence of an acid catalyst, suggesting thereby that the cis-trans isomerisation of (11d) may not be taking place under these conditions to any appreciable extent.

In continuation of our studies, we have examined the thermal and photochemical transformation of a bisphenylazoalkene such as 1,2-bisphenylazoacenaphthylene (47). Direct heating of (47) as in the earlier cases did not give rise to any triazole. However, when (47) was photolysed in a mixture of methanol and methylene chloride, a 17% yield of acenaphthene-

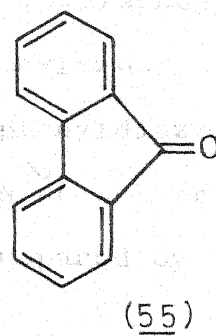
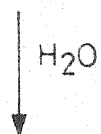
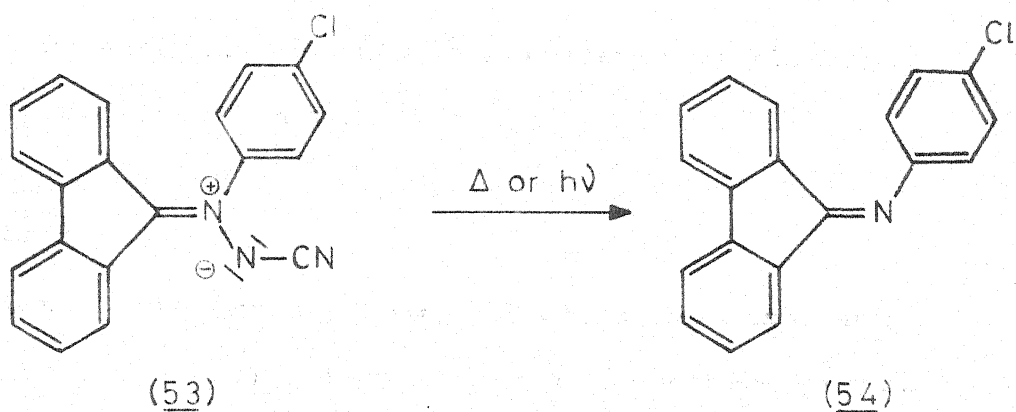
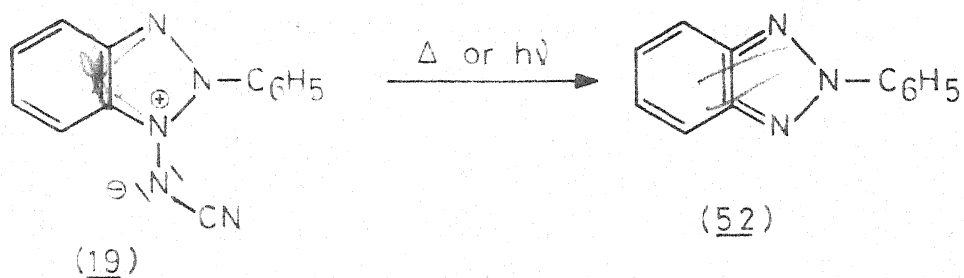


quinone monophenylhydrazone (51) was obtained. The exact mechanism of this transformation is not clear. However, one of the possibilities would involve the addition of methanol under photolytic condition to (47), to give (48) which will homolytically fragment to (49) and then ultimately be converted to (51), perhaps through an intermediate like (50) (Scheme 2.10).

In continuation, we have examined the thermal and photochemical transformations of two related azomethine imines, namely, o-phenylazophenyldiazocyanide which can exist as anhydro 1-cyanoimino-2-phenyl-4,5-benzo-1,2,3-triazolium hydroxide (19) and C-biphenylene-N ^{α} -(p-chlorophenyl)-N ^{β} -cyanoazomethineimine (53). Heating of (19) in the absence of any solvent around 150-160° for 3 hr gave a 47% yield of a product melting at 110° and identified as 2-phenyl-4,5-benzo-1,2,3-triazole (52). The same triazole (52) was obtained in a 55% yield when a benzene solution of (19) was photolysed for 2 hr. The thermal transformation of 53, however, gave a mixture of products consisting of 9-fluorenone (4-chlorophenyl) anil (54) and 9-fluorenone (55). Photolysis of (53), on the other hand, gave a much better yield of (54) (Scheme 2.11).

The formation of the triazole (52) and the anil (54) in the reactions of (19) and (53), respectively, may be

Scheme 2.11



rationalised in terms of the loss of cyanonitrene from the starting azomethineimines. However, our attempts to trap this nitrene in these reactions have not been successful. The formation of 9-fluorenone (55) in the thermolysis of (49), on the other hand, may be due to a hydrolytic fragmentation of the anil (55), under the reaction conditions, or subsequent work-up of the reaction mixture.

2.3 EXPERIMENTAL

All melting points are uncorrected. All irradiation experiments were carried out using a Hanovia, medium-pressure, mercury lamp (450 W). Nmr spectra were recorded on a Varian A60D, NMR Spectrometer and infrared spectra on a Perkin-Elmer Model 521, Infrared Spectrometer.

Starting Materials

Oxidation of the corresponding 1,2-diketone bisphenylhydrazones employing nickel peroxide as per a reported procedure³ gave 1,2-bisphenylazostilbene (10a), mp 179° (60%), 1,2-bisphenylazodi(4-chlorophenyl)ethylene (10b), mp 205° (87%), 1,2-bisphenylazodi(4-methoxyphenyl)ethylene (10c), mp 175° (31%), 1,2-bisphenylazoethylene, (10d), mp 149° (93%), 2,3-bisphenylazo-2-butene, (10e), mp 159° (85%) and 1,2-bisphenylazo-acenaphthylene (47), mp 180° (96%). *o*-Phenylazophenyldiazocyanide (19),¹⁵ mp 158° (60%) and C-biphenylene-N[∞]-(4-chloro)phenyl-N^β-cyanoazomethineimine,²⁹ mp 194° were prepared by reported procedures.

Preparation of 1,2-Bisphenylazocyclohexene (40)

A mixture of 4 g (0.013 mol) of cyclohexane-1,2-dione bisphenylhydrazone (39) and 12 g of nickel peroxide in 200 ml benzene was stirred for 4 hr at room temperature. Removal of the inorganic material and solvent gave a viscous mass which was recrystallised from a mixture (1:1) of petroleum ether (bp 60-80) and benzene to give 3.2 g (82%) of 1,2-bisphenylazocyclohexene (40) mp 127-128°.

Anal. Calcd for $C_{18}H_{14}N_4$: C, 74.48; H, 6.21, N, 19.31. Found C, 74.61; H, 6.29; N, 19.31.

Thermolysis of 1,2-Bisphenylazostilbene (10a)

Bisphenylazostilbene (10a), (0.2 g, 0.005 mol) was heated around 175°-180° in a sealed tube in an oil bath for 15 minutes and the product mixture was chromatographed over alumina. Elution with petroleum ether (bp 60-80°) gave 0.13 g (85%) of 2,4,5-triphenyl-1,2,3-triazole, (13a), mp 124° (mmp).²²

Photolysis of 1,2-Bisphenylazostilbene (10a)

A solution of 0.2 g of (10a) in 175 ml benzene was irradiated for 2 hr. Removal of the solvent under reduced pressure gave a viscous residue which was chromatographed over alumina. Elution with petroleum ether (bp 60-80°) gave 0.11 g (61%) 2,4,5-triphenyl-1,2,3-triazole, (13a) mp 124° (mmp).

Thermolysis of 1,2-Bisphenylazobis(4-chlorophenyl)ethylene (10b)

1,2-Bisphenylazobis(4-chlorophenyl)ethylene (10b) (0.2 g, 0.5 mmol) was heated in a sealed tube in an oil-bath around 205-210° for 1 hr and the reaction product was chromatographed over alumina. Elution with petroleum ether (bp 60-80°) gave 90 mg (55%) of 2-phenyl-4,5-di-(4-chlorophenyl)-1,2,3-triazole, (13b), mp 155° (mmp).³

Photolysis of 1,2-Bisphenylazobis(4-chlorophenyl)ethylene (10b)

A solution of (10b) (0.2 g, 0.5 mmol) in 175 ml benzene was irradiated for 1 hr. Subsequent removal of the solvent gave a residue which was chromatographed over alumina. Elution with petroleum ether (bp 60-80°) gave 90 mg (55%) of 2-phenyl-4,5-di-(4-chlorophenyl)-1,2,3-triazole, (13b) mp 155° (mmp).

Thermolysis of 1,2-Bisphenylazobis(4-methoxyphenyl)ethylene (10c)

Heating (10c) (0.2 g, 0.5 mmol) around 170-180° for 1 hr and subsequently chromatographing the reaction product over alumina, using petroleum ether (bp 60-80°) gave 110 mg (60%) of 2-phenyl-4,5-di(4-methoxyphenyl)-1,2,3-triazole, (13c), mp 134° (mmp).³

Photolysis of 1,2-Bisphenylazobis(4-methoxyphenyl)ethylene (10c)

A solution of (10c) (0.2 g, 0.5 mmol) in 175 ml benzene

was irradiated for 2 hr. Removal of the solvent under reduced pressure and chromatographing the residue on alumina, using petroleum ether (bp 60-80°) gave 12 mg (17%) of biphenyl, mp 70° (mmp). Continued elution with a mixture (3:1) of petroleum ether (bp 60-80°) and benzene, gave 140 mg (89%) of 2-phenyl-4,5-di(4-methoxyphenyl)-1,2,3-triazole (13c), mp 134° (mmp).³

Thermolysis of 1,2-Bisphenylazocyclohexene (40)

Heating 1,2-bisphenylazocyclohexene (40) (0.29 g, 1 mmol) around 125-130° for 1 hr and subsequent chromatography of the reaction product over alumina using petroleum ether (bp 60-80°) gave 20 mg (14%) of 2-phenyl-4,5-tetramethylene-1,2,3-triazole (42), mp 89-90°, after recrystallization from petroleum ether (bp 60-80°).

Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.36; H, 6.53; N, 21.12; Mol. wt., 199. Found: C, 72.24; H, 6.1; N, 20.75; Mol. wt., 199 (mass spectrometry).

The nmr spectrum of (42) in $CDCl_3$ showed multiplets around 1.90 δ (4 H) and 2.81 δ (4HH) due to the methylene protons and at 7.45 δ (5 H) due to phenyl protons.

Photolysis of 1,2-Bisphenylazocyclohexene (40)

A solution of (40) (200 mg, 0.6 mmol) in 175 ml benzene was irradiated for 8 hr. Removal of the solvent under reduced

pressure and chromatography of the residue over alumina using petroleum ether (bp 60-80°) gave 10 mg (10%) of biphenyl, mp 70 (mmp). Continued elution with the same solvent gave 40 mg (28%) of 2-phenyl-4,5-tetramethylene-1,2,3-triazole, (42), mp 90° (mmp).

Further elution with a mixture (1:1) of benzene and petroleum ether (bp 60-80°) gave 10 mg (5% of 1-anilino-2-phenyl-1,4,5,6-tetrahydrocyclohexa[d] 1,2,3-triazole (43), mp 136°.

Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.48; H, 6.20; N, 19.3; Mol. wt., 290. Found: C, 74.70; H, 5.9; N, 19.17; Mol. wt., 290 (Mass spectrometry).

The nmr spectrum of (43) in $CDCl_3$ showed peaks around 2.15 δ (4 H,m) and 2.95 δ (2 H,m) due to the methylene protons, a broad peak at 3.75 δ (1 H) due to the NH proton, a multiplet at 4.35 δ (1 H) due to the vinylic proton and a multiplet spread over the range of 7.0-8.0 δ due to the phenyl protons (10 H). The broad peak at 3.75 δ disappeared on D_2O exchange.

Attempted Photolysis and Thermolysis of 1,2-Bisphenylazoethylene (10d) and 2,3-Bisphenylazo-2-butene (10e)

Heating 200 mg (0.83 mmol) of 1,2-bisphenylazoethylene (10d) around 160° for 4 hr and subsequent work-up as in the earlier cases gave 190 mg (95%) of the unchanged starting

material, mp 149° (mmp).

Irradiation for 6 hr of a solution of (10d) (200 mg, 0.83 mmol) in 175 ml benzene, and work-up as in the earlier cases gave 180 mg (90%) of the unchanged starting material, mp 149° (mmp).

Similarly, heating 200 mg (0.78 mmol) of 2,3-bisphenyl-azo-2-butene (10e) around 170° for 4 hr and subsequent work-up gave 175 mg (87%) of the unchanged starting material, mp 159° (mmp). Irradiation of a solution of (10e) (200 mg, 0.78 mmol) in 175 ml benzene for 8 hr and subsequent work-up gave 185 mg (92%) of the unchanged starting material, mp 159° (mmp).

Photolysis of 2,3-Bisphenylazo-2-butene (10e) in Presence of Dry Hydrogen Chloride

A solution of 260 mg (1 mmol) of (10e) in 175 ml of dry benzene was irradiated for 10 minutes while a continuous stream of dry hydrogen chloride was passed through the solution. The solution was subsequently washed with water to remove all hydrochloric acid and the solvent was removed under vacuum to give a product which was chromatographed over alumina. Elution with petroleum ether (bp 60-80°) gave 110 mg (60%) of 2-phenyl-4,5-dimethyl-1,2,3-triazole (46), bp 160°/60 mm, identified through a comparison of its ir spectrum with that of an authentic sample.⁵

Photolysis of 1,2-Bisphenylazoacenaphthylene (47)

A solution of 440 mg (1.5 mmol) of 1,2-bisphenylazoacenaphthylene (47) in 175 ml of a mixture (1:1) of methylene chloride and methanol was irradiated for 6 hr. Removal of the solvent gave a viscous residue which when chromatographed over alumina gave 55 mg (17%) of 1,2-acenaphthenequinone monophenylhydrazone (51), mp 179-80° (mmp).

Thermolysis of o-Phenylazophenyldiazocyanide (19)

Heating 200 mg (0.85 mmol) of (19) around 150-160° for 3 hr followed by chromatography of the reaction product over alumina using petroleum ether (bp 60-80°) gave 70 mg (47%) of 2-phenyl-4,5-benzo-1,2,3-triazole (52), mp 110° (mmp).¹⁵

Photolysis of o-Phenylazophenyldiazocyanide (19)

A solution of 200 mg (0.85 mmol) of (19) in 175 ml of benzene was irradiated for 2 hr. Removal of the solvent under vacuum and chromatographing the residue over alumina using petroleum ether (bp 60-80°) gave 90 mg (55%) of 2-phenyl-4,5-benzo-1,2,3-triazole (52), mp 110° (mmp).

Thermolysis of C-Biphenylene-N^α-(4-chlorophenyl)-N^β-cyano-azomethineimine (53)

Heating 0.15 g (0.45 mmol) of (53) around 200-210° for 1 hr followed by chromatography of the reaction product over

alumina using petroleum ether (bp 60-80°) gave 15 mg (11%) of 9-fluorenone (4-chlorophenyl) anil, (54), mp 150° (mmp).

Continued elution with a mixture (1:1) of benzene and petroleum ether (bp 60-80°) gave 10 mg (12%) of 9-fluorenone, (55), mp 83-84° (mmp).

Photolysis of C-Biphenylene-N^α-(4-chlorophenyl)-N^β-cyano-azomethine imine (53)

A solution of (53) (0.15 g, 0.45 mmol) in 175 ml benzene was irradiated for 2 hr. Removal of the solvent under vacuum gave a dark tarry mass which was repeatedly extracted with benzene. Removal of the solvent from the extract and chromatography of the residue gave 42 mg (32%) of 9-fluorenone-(4-chlorophenyl) anil (54), mp 150° (mmp).

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CHAPTER 3

1,3-DIPOLAR CYCLOADDITIONS OF 1,2-BISPHENYLAZOALKENES

3.1 ABSTRACT

Bisphenylazostilbene (2a), the oxidation product of benzilbisphenylhydrazone, has been shown to behave as the mesoionic anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide (3a), in its reactions with a variety of acetylenic and olefinic dipolarophiles. Thus, pyrazolino[2,3-c][1,2,3] triazoles were formed in the reaction of 2a with dimethyl acetylenedicarboxylate, methyl propiolate and dibenzoylacetylene. Similarly,

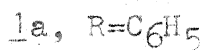
dihydropyrazolino[2,3-c][1,2,3]triazoles were formed in excellent yields in the reaction of 2a with dimethyl fumarate, dimethyl maleate, trans-dibenzoyl ethylene, maleic anhydride, methyl crotonate, methyl methacrylate, ethyl acrylate and acrylonitrile. With phenyl isocyanate and phenyl isothiocyanate, 2a gave 1,3,3a,4,6-pentaphenyl-1,2,4-triazolidino[1,5-c][1,2,3]triazol-5-one and the corresponding thione, respectively. With carbon disulphide, the initially formed cycloadduct fragmented to give 2,4,5-triphenyl-1,2,3-triazole, phenyl isothiocyanate and elemental sulphur. The stereospecificity and regioselectivity of these cycloadditions have been established by an examination of the nmr spectra of a number of these cycloadducts. Study of the kinetics of some of these additions has shown that the Eyring parameters of these reactions are of the same order as the corresponding values in other typical 1,3-dipolar cycloaddition reactions. Similar cycloaddition reactions have been carried out with other 1,2-bisphenylazoalkenes like 1,2-bisphenylazodi(4-chlorophenyl)ethylene (2b), 1,2-bisphenylazodi(4-methoxyphenyl)ethylene (2c) and 1,2-bisphenylazocyclohexene (26). The cycloadducts obtained in the reaction of 1,2-bisphenylazostilbene with dimethyl maleate and dimethyl fumarate on thermolysis gave, 2,4,5-triphenyl-1,2,3-triazole, in both cases.

3.2 RESULTS AND DISCUSSION

In Chapter 2, we have stated that nitrileimines could undergo dimerization to give bisazoalkenes. Also, we have indicated that bisazoalkenes can be conveniently prepared through the oxidation of the corresponding bisphenylhydrazones of 1,2-diketones employing non-stoichiometric oxides such as nickel peroxide. The results of our studies concerning the thermal and photochemical fragmentation of bisphenylazoalkenes suggested the possible existence of an equilibrium between the different valence isomers of the type shown in Scheme 3.1.

A structure such as 3 incorporates an azomethineimine moiety and as such should be expected to undergo 1,3-dipolar cycloaddition reactions. In view of the synthetic potential of such reactions, we thought it worthwhile to make a detailed investigation of the reactions of bisphenylazoalkenes with a number of acetylenic and olefinic dipolarophiles. Since the equilibrium concentrations of various possible valence tautomers are likely to be dependent on the stereochemical features of the starting bisphenylazoalkenes themselves, we have attempted at a correlation between the structure and dipolar activity of bisphenylazoalkenes.

Bisphenylazostilbene has been reported to be formed as one of the products of oxidation of benzilbisphenylhydrazone when nickel peroxide or a mixture of sodium ethoxide

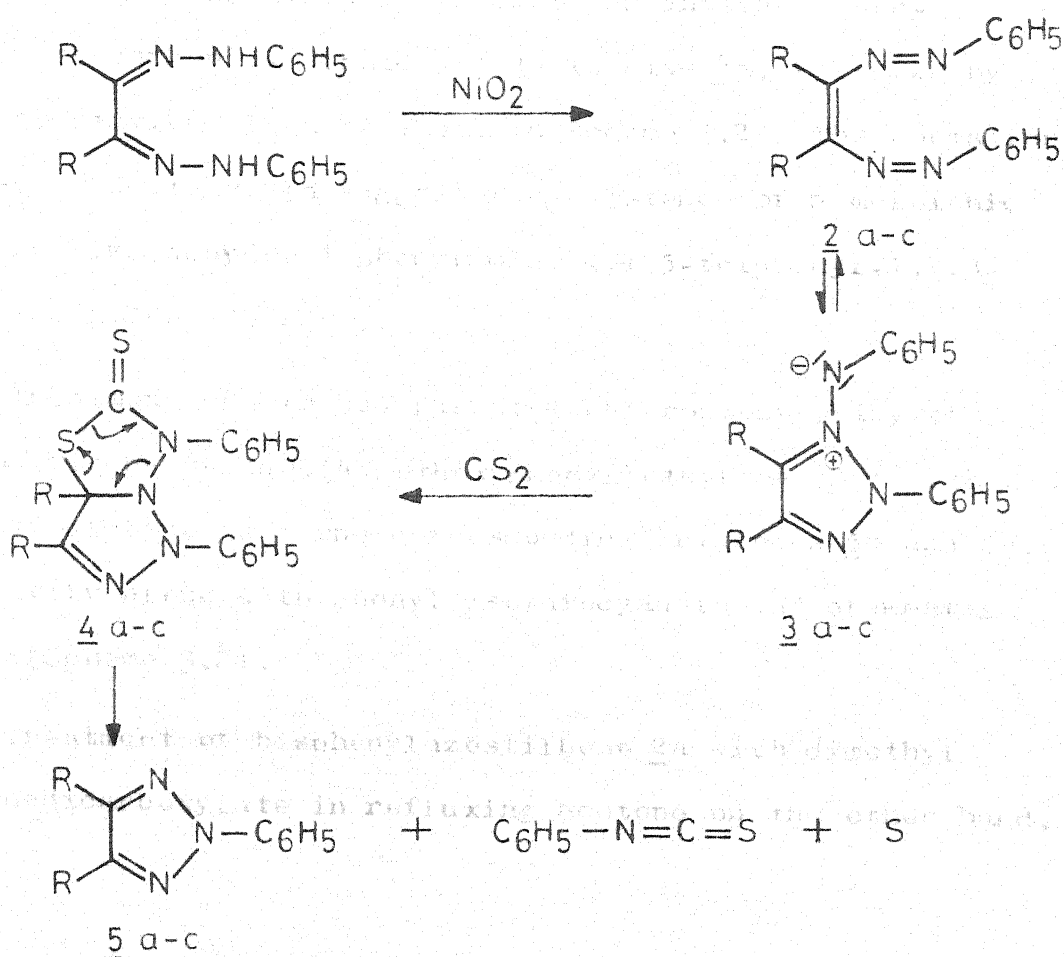


2450

3 a-c

b, R=p-Cl-C₆H₄

c, R=p-CH₃O-C₆H₄



and iodine is used as the oxidising agent.^{2,3} In view of the excellent yields of bisazoalkenes obtained by the nickel peroxide oxidation of 1,2-diketone bisphenylhydrazones this method was employed in the preparation of all bisphenylazoalkenes which were investigated by us.

Treatment of bisphenylazostilbene (2a) with carbon disulphide at room temperature gave a 93% yield of 2,4,5-triphenyl-1,2,3-triazole (5a). In addition, a 83% yield of elemental sulphur and 66% yield of phenyl isothiocyanate were also isolated in this reaction. The formation of all these products can be explained in terms of an initial cycloaddition of carbon disulphide to 3a to give 4a, followed by the fragmentation of 4a as shown in Scheme 3.2. The formation of these products would suggest the existence of a mesoionic structure like anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide (3a).

Treatment of bisphenylazodi(4-chlorophenyl)ethylene (2b) and bisphenylazodi(4-methoxyphenyl)ethylene (2c) with carbon disulphide gave the corresponding triazoles 5b and 5c, respectively along with phenyl isothiocyanate and elemental sulphur (Scheme 3.2).

Treatment of bisphenylazostilbene 2a with dimethyl acetylenedicarboxylate in refluxing acetone on the other hand,

gave a 83% yield of a 1:1-adduct, mp 184° and identified as 1,3,3a,6-tetraphenyl-4,5-dicarbomethoxypyrazolino [2,3-c] [1,2,3]-triazole (7a). The nmr spectrum of (7a) (Fig. 3.1) showed two sharp singlets at 3.46δ (3 H) and 3.66δ (3 H), respectively, due to the two sets of ester methyl protons. The phenyl protons appeared as a multiplet spread over the range of $6.70-7.30 \delta$ (20 H). The ir characteristics of this pyrazolino-triazole and other similar compounds are discussed elsewhere in this chapter.

Similarly, the treatment of 2b with dimethyl acetylenedicarboxylate gave the expected 2,6-diphenyl-3,3a-di(4-chlorophenyl)-4,5-dicarbomethoxypyrazolino [2,3-c] [1,2,3] triazole (7b). On the other hand, treatment of 2c with dimethyl acetylenedicarboxylate gave 2,6-diphenyl-3,3a-di(4-methoxyphenyl)-4,5-dicarbomethoxypyrazolino [2,3-c] [1,2,3] triazole (7c) (Scheme 3.3).

The nmr spectrum of 7b showed two singlets at 3.70δ (3 H) and 3.90δ (3 H) due to the ester methyl protons. The phenyl protons appeared as two sets of multiplets over the ranges $7.10-7.80 \delta$ (16 H) and at 8.50δ (2 H). The nmr spectrum of 7c showed four singlets at 3.68δ (3 H), 3.72δ (3 H), 3.78δ (3 H) and 3.92δ (3 H), respectively, due to the four methoxy groups present in 7c. The phenyl protons appeared as two sets of multiplets, one spread over the range $6.58-7.75 \delta$ (16 H) and the other around 8.58δ (2 H).

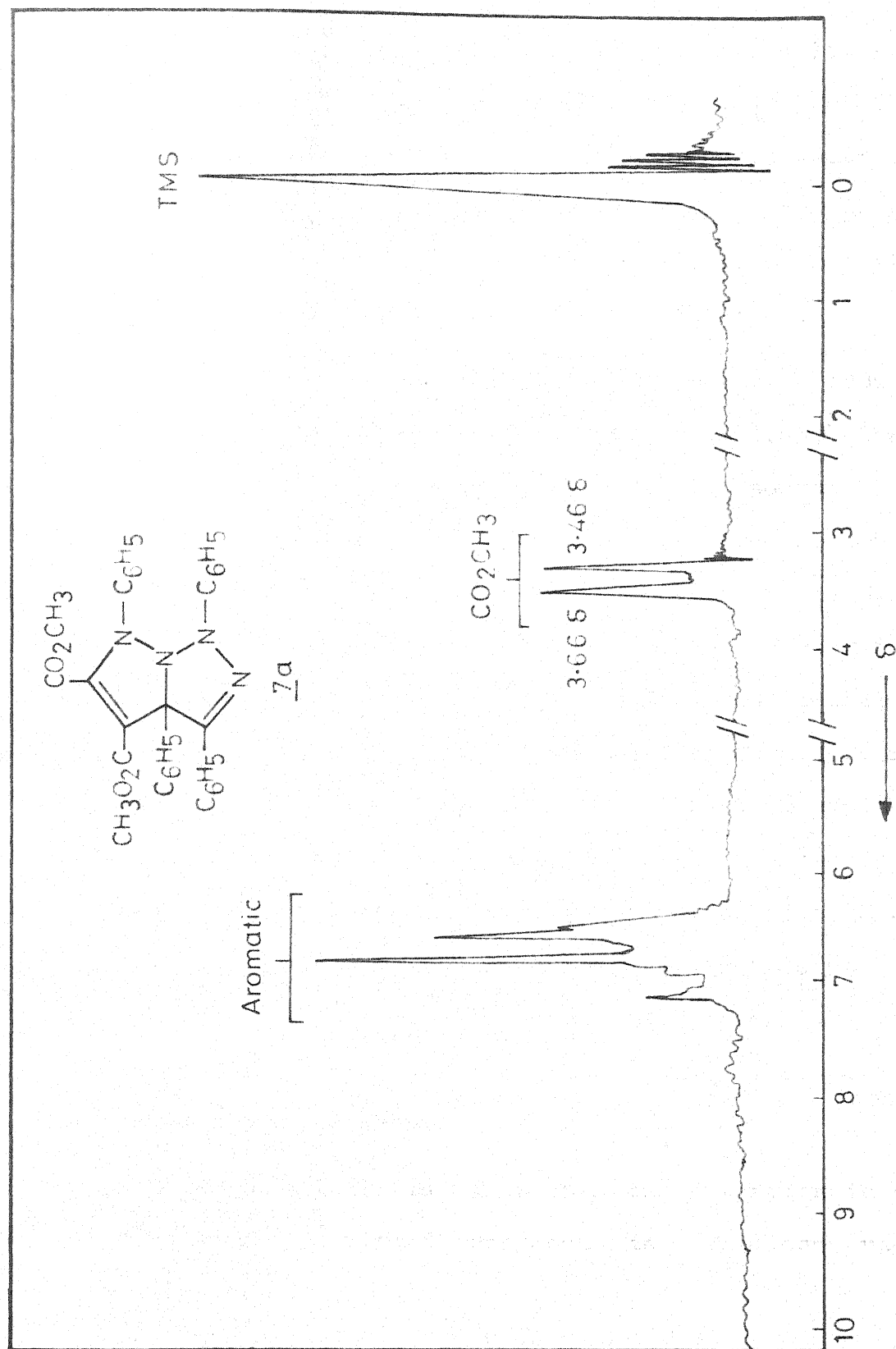


Fig. 3.1 Nmr Spectrum (100 MHz) of 1,3,3a,6-Tetraphenyl-4,5-dicarbomethoxy-pyrazolino[2,3-c][1,2,3]triazole (**7a**)

Reaction of methyl propiolate with 2a gave a 78% yield of 1,3,3a,6-tetraphenyl-4-carbomethoxypyrazolino[2,3-c][1,2,3]-triazole (8a). The corresponding 1,6-diphenyl-3,3a-diaryl-4-carbomethoxypyrazolino[2,3-c][1,2,3] triazoles, 8b and 8c were obtained in 55% and 38% yields from the reaction of methyl propiolate with 2b and 2c respectively (Scheme 3.3).

The nmr spectrum of one of the representative adducts, 8b (Fig. 3.2), for example, showed a singlet at 3.63 δ (3 H) due to the ester methyl protons and a multiplet spread over the range of 7.00-8.80 δ (18 H) due to the aromatic protons. In addition, the spectrum showed a singlet at 8.58 δ (1 H) due to the vinylic proton at C₅-position. An alternative structural representation for the adduct formed in the reaction of 3b with methyl propiolate is 8b', arising through a different mode of addition (Scheme 3.5). With a view to distinguishing between these two structures, we have compared the chemical shift of the vinylic proton in this adduct with the chemical shifts of the vinylic protons in analogous β -amino- α,β -unsaturated carbonyl systems. Table 3.1 summarizes the chemical shifts of both α and β protons in some representative β -amino α,β -unsaturated carbonyl systems.

From Table 3.1, it is clear that the β -proton in each of these enamines is shifted more down-field when compared to

Table 3.1

Chemical Shifts of α and β Protons in Some β -Dimethylamino- α,β -unsaturated Carbonyl Systems^{4,5}

Compound	Chemical Shift in ppm	
	α -Proton	β - Proton
$(\text{CH}_3)_2\text{N}-\text{CH}=\text{CH}-\text{CHO}$	5.7*	7.12*
$(\text{CH}_3)_2\text{N}-\text{CH}=\overset{\text{CHO}}{\underset{ }{\text{C}}}-\text{CH}_3$		6.58
$(\text{CH}_3)_2\text{N}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	4.87*	6.97*
$(\text{CH}_3)_2\text{N}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5$	5.57	7.60
$(\text{CH}_3)_2\text{N}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$	4.36	7.29
$\text{C}_6\text{H}_5-\overset{\text{CH}_3}{\underset{ }{\text{N}}}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$	4.85	7.82

*The authors have not specified the stereochemistry about the C=C bond, in these compounds.

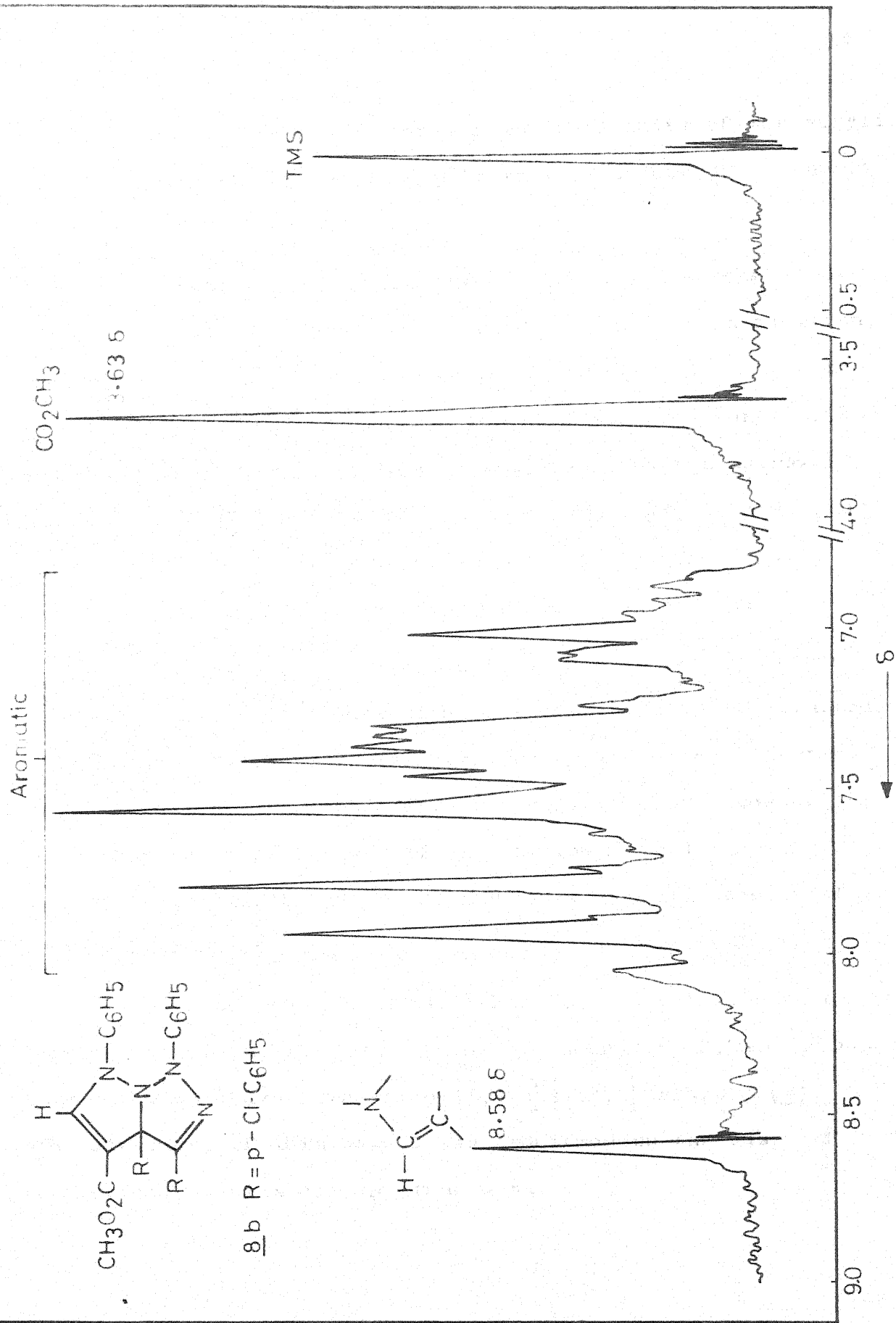


Fig. 3.2 Nmr Spectrum (60 MHz) of 1,6-Diphenyl-3,3a-di(p-chlorophenyl)-4-carbomethoxy-

the α -proton. The rather large down-field shift of the vinylic proton in our adduct would suggest that structure 8b correctly represents this compound.

Similarly, the nmr spectrum of 8c showed a singlet at 8.63 δ due to the vinylic proton at C₅-position. In addition, the spectrum of 8c showed a singlet at 3.64 δ (3 H) due to the ester methyl protons, a multiplet spread over the range 6.92 - 8.16 δ (18 H) due to the aromatic protons. The two methoxyl protons attached to the phenyl groups at C₃ and C_{3a}-positions appeared together as a singlet at 3.92 δ (6 H). Table 3.2 summarises the nmr spectral features of these adducts.

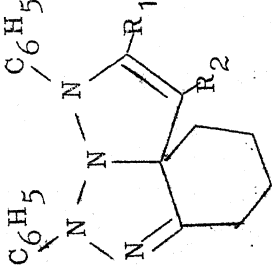
The formation of products like 8a-c in the reactions of 1,2-bisphenylazoalkenes with an asymmetrically substituted dipolarophile such as methyl propiolate, would indicate that these reactions are proceeding in a regioselective manner such that the negative end of the intermediate 1,3-dipolar system is getting bound to the most electrophilic center of the dipolarophile.

The reaction of bisphenylazostilbene (2a) with dibenzoylacetylene gave a 64% yield of the 1:1-adduct, 1,3,3a,6-tetraphenyl-4,5-dibenzoylpyrazolino [2,3-c] [1,2,3] triazole (9). The structure of this adduct was confirmed on the basis of analytical results and spectral data.

Nmr Spectral Characteristics of Pyrazolino[2,3-c][1,2,3]-triazoles

C6H5C1=CC=C(C=C1)N2C(=C(C=C2)N3C(=CC(=C3)N4C(=CC(=C4)N5C(=CC(=C5)N6C(=CC(=C6)N7C(=CC(=C7)N8C(=CC(=C8)N9C(=CC(=C9)N10C(=CC(=C10)N11C(=CC(=C11)N12C(=CC(=C12)N13C(=CC(=C13)N14C(=CC(=C14)N15C(=CC(=C15)N16C(=CC(=C16)N17C(=CC(=C17)N18C(=CC(=C18)N19C(=CC(=C19)N20C(=CC(=C20)N21C(=CC(=C21)N22C(=CC(=C22)N23C(=CC(=C23)N24C(=CC(=C24)N25C(=CC(=C25)N26C(=CC(=C26)N27C(=CC(=C27)N28C(=CC(=C28)N29C(=CC(=C29)N30C(=CC(=C30)N31C(=CC(=C31)N32C(=CC(=C32)N33C(=CC(=C33)N34C(=CC(=C34)N35C(=CC(=C35)N36C(=CC(=C36)N37C(=CC(=C37)N38C(=CC(=C38)N39C(=CC(=C39)N40C(=CC(=C40)N41C(=CC(=C41)N42C(=CC(=C42)N43C(=CC(=C43)N44C(=CC(=C44)N45C(=CC(=C45)N46C(=CC(=C46)N47C(=CC(=C47)N48C(=CC(=C48)N49C(=CC(=C49)N50C(=CC(=C50)N51C(=CC(=C51)N52C(=CC(=C52)N53C(=CC(=C53)N54C(=CC(=C54)N55C(=CC(=C55)N56C(=CC(=C56)N57C(=CC(=C57)N58C(=CC(=C58)N59C(=CC(=C59)N60C(=CC(=C60)N61C(=CC(=C61)N62C(=CC(=C62)N63C(=CC(=C63)N64C(=CC(=C64)N65C(=CC(=C65)N66C(=CC(=C66)N67C(=CC(=C67)N68C(=CC(=C68)N69C(=CC(=C69)N70C(=CC(=C70)N71C(=CC(=C71)N72C(=CC(=C72)N73C(=CC(=C73)N74C(=CC(=C74)N75C(=CC(=C75)N76C(=CC(=C76)N77C(=CC(=C77)N78C(=CC(=C78)N79C(=CC(=C79)N80C(=CC(=C80)N81C(=CC(=C81)N82C(=CC(=C82)N83C(=CC(=C83)N84C(=CC(=C84)N85C(=CC(=C85)N86C(=CC(=C86)N87C(=CC(=C87)N88C(=CC(=C88)N89C(=CC(=C89)N90C(=CC(=C90)N91C(=CC(=C91)N92C(=CC(=C92)N93C(=CC(=C93)N94C(=CC(=C94)N95C(=CC(=C95)N96C(=CC(=C96)N97C(=CC(=C97)N98C(=CC(=C98)N99C(=CC(=C99)N100C(=CC(=C100)N101C(=CC(=C101)N102C(=CC(=C102)N103C(=CC(=C103)N104C(=CC(=C104)N105C(=CC(=C105)N106C(=CC(=C106)N107C(=CC(=C107)N108C(=CC(=C108)N109C(=CC(=C109)N110C(=CC(=C110)N111C(=CC(=C111)N112C(=CC(=C112)N113C(=CC(=C113)N114C(=CC(=C114)N115C(=CC(=C115)N116C(=CC(=C116)N117C(=CC(=C117)N118C(=CC(=C118)N119C(=CC(=C119)N120C(=CC(=C120)N121C(=CC(=C121)N122C(=CC(=C122)N123C(=CC(=C123)N124C(=CC(=C124)N125C(=CC(=C125)N126C(=CC(=C126)N127C(=CC(=C127)N128C(=CC(=C128)N129C(=CC(=C129)N130C(=CC(=C130)N131C(=CC(=C131)N132C(=CC(=C132)N133C(=CC(=C133)N134C(=CC(=C134)N135C(=CC(=C135)N136C(=CC(=C136)N137C(=CC(=C137)N138C(=CC(=C138)N139C(=CC(=C139)N140C(=CC(=C140)N141C(=CC(=C141)N142C(=CC(=C142)N143C(=CC(=C143)N144C(=CC(=C144)N145C(=CC(=C145)N146C(=CC(=C146)N147C(=CC(=C147)N148C(=CC(=C148)N149C(=CC(=C149)N150C(=CC(=C150)N151C(=CC(=C151)N152C(=CC(=C152)N153C(=CC(=C153)N154C(=CC(=C154)N155C(=CC(=C155)N156C(=CC(=C156)N157C(=CC(=C157)N158C(=CC(=C158)N159C(=CC(=C159)N160C(=CC(=C160)N161C(=CC(=C161)N162C(=CC(=C162)N163C(=CC(=C163)N164C(=CC(=C164)N165C(=CC(=C165)N166C(=CC(=C166)N167C(=CC(=C167)N168C(=CC(=C168)N169C(=CC(=C169)N170C(=CC(=C170)N171C(=CC(=C171)N172C(=CC(=C172)N173C(=CC(=C173)N174C(=CC(=C174)N175C(=CC(=C175)N176C(=CC(=C176)N177C(=CC(=C177)N178C(=CC(=C178)N179C(=CC(=C179)N180C(=CC(=C180)N181C(=CC(=C181)N182C(=CC(=C182)N183C(=CC(=C183)N184C(=CC(=C184)N185C(=CC(=C185)N186C(=CC(=C186)N187C(=CC(=C187)N188C(=CC(=C188)N189C(=CC(=C189)N190C(=CC(=C190)N191C(=CC(=C191)N192C(=CC(=C192)N193C(=CC(=C193)N194C(=CC(=C194)N195C(=CC(=C195)N196C(=CC(=C196)N197C(=CC(=C197)N198C(=CC(=C198)N199C(=CC(=C199)N200C(=CC(=C200)N201C(=CC(=C201)N202C(=CC(=C202)N203C(=CC(=C203)N204C(=CC(=C204)N205C(=CC(=C205)N206C(=CC(=C206)N207C(=CC(=C207)N208C(=CC(=C208)N209C(=CC(=C209)N210C(=CC(=C210)N211C(=CC(=C211)N212C(=CC(=C212)N213C(=CC(=C213)N214C(=CC(=C214)N215C(=CC(=C215)N216C(=CC(=C216)N217C(=CC(=C217)N218C(=CC(=C218)N219C(=CC(=C219)N220C(=CC(=C220)N221C(=CC(=C221)N222C(=CC(=C222)N223C(=CC(=C223)N224C(=CC(=C224)N225C(=CC(=C225)N226C(=CC(=C226)N227C(=CC(=C227)N228C(=CC(=C228)N229C(=CC(=C229)N230C(=CC(=C230)N231C(=CC(=C231)N232C(=CC(=C232)N233C(=CC(=C233)N234C(=CC(=C234)N235C(=CC(=C235)N236C(=CC(=C236)N237C(=CC(=C237)N238C(=CC(=C238)N239C(=CC(=C239)N240C(=CC(=C240)N241C(=CC(=C241)N242C(=CC(=C242)N243C(=CC(=C243)N244C(=CC(=C244)N245C(=CC(=C245)N246C(=CC(=C246)N247C(=CC(=C247)N248C(=CC(=C248)N249C(=CC(=C249)N250C(=CC(=C250)N251C(=CC(=C251)N252C(=CC(=C252)N253C(=CC(=C253)N254C(=CC(=C254)N255C(=CC(=C255)N256C(=CC(=C256)N257C(=CC(=C257)N258C(=CC(=C258)N259C(=CC(=C259)N260C(=CC(=C260)N261C(=CC(=C261)N262C(=CC(=C262)N263C(=CC(=C263)N264C(=CC(=C264)N265C(=CC(=C265)N266C(=CC(=C266)N267C(=CC(=C267)N268C(=CC(=C268)N269C(=CC(=C269)N270C(=CC(=C270)N271C(=CC(=C271)N272C(=CC(=C272)N273C(=CC(=C273)N274C(=CC(=C274)N275C(=CC(=C275)N276C(=CC(=C276)N277C(=CC(=C277)N278C(=CC(=C278)N279C(=CC(=C279)N280C(=CC(=C280)N281C(=CC(=C281)N282C(=CC(=C282)N283C(=CC(=C283)N284C(=CC(=C284)N285C(=CC(=C285)N286C(=CC(=C286)N287C(=CC(=C287)N288

Table 3.2 (...Contd.)

(i)	(ii)	(iii)	(iv)	(v)	(vi)
					
<u>29</u> , R ₁ = R ₂ = CO ₂ CH ₃	3.78	3.83	7.46 - 8.41		1.35-2.60 ^b
<u>30</u> , R ₁ = H, R ₂ = CO ₂ CH ₃	3.87		7.25 - 8.43	7.80	1.30-2.65 ^b

a) Signals due to p-OCH₃ substituent of phenyl groups at C₃- and C_{3a}-positions.

b) Signal due to the four methylene groups bridging C₃- and C_{3a}-positions.

Diels-Alder additions, 1,3-dipolar cycloaddition reactions and various other concerted processes are characterised by their stereospecificity. We have, in continuation of our studies, examined the reaction of bisphenylazostilbene (2a) with olefinic substrates with a view to understanding the stereochemical outcome of these reactions. Treatment of 2a with dimethyl maleate in acetone medium gave a single 1:1-adduct (79%), identified as cis-4,5-dicarbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c][1,2,3]triazole (10a). The nmr spectrum of 10a (Fig. 3.3) showed two singlets at 3.69 δ (3 H) and 3.07 δ (3H) respectively, due to ester methyl protons. The signal due to the phenyl protons appeared as three sets of multiplets at 6.67 δ (14 H), 7.17 δ (4 H) and 8.00 δ (2 H). The two tertiary protons appeared as two sets of doublets at 3.88 δ (1 H) and 4.41 δ (1 H), respectively ($J = 9.7$ Hz). The dihedral angle calculated from the coupling constant using the modified Karplus equation,⁶

$$J_{HH} = 0.985 - 2.975 \cos \phi + 15.488 \cos^2 \phi$$

comes out to be 32° , thereby indicating that the two hydrogens are cis with respect to each other, as would be expected in a stereospecific addition of 2a to dimethyl maleate.

Reactions of both 2b and 2c with dimethyl maleate gave the corresponding stereospecific addition products, cis-4,5-dicarbomethoxy-1,6-diphenyl-3,3a-di(4-chlorophenyl)-4,5-

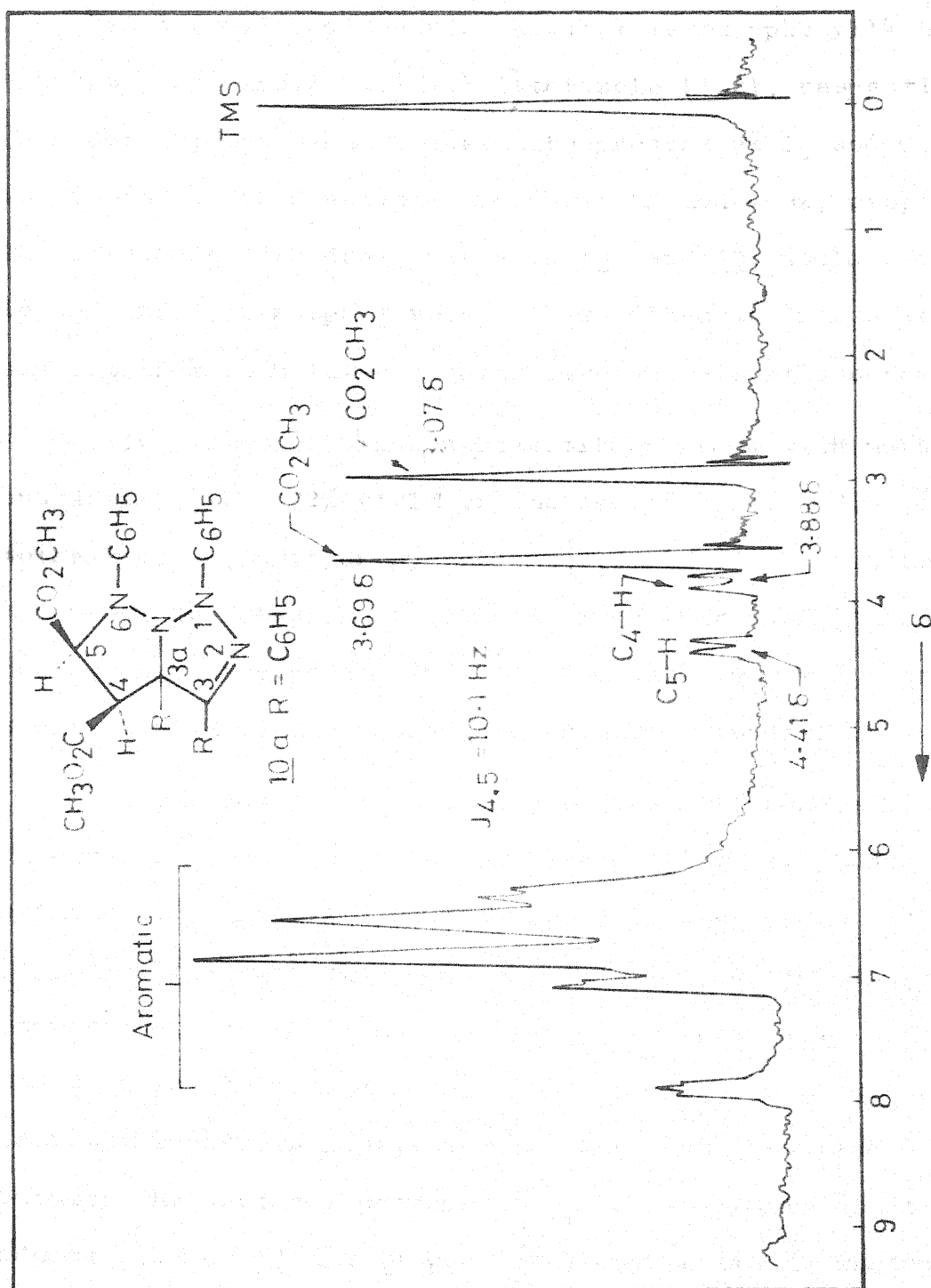


Fig. 3.3 Nmr Spectrum (100 MHz) of *cis*-4,5-dihydro-4,5-dicarboethoxy-1,3,3a,6-tetraphenylpyrazolino [2,3-*c*] [1,2,3] triazole (**10a**)

dihydropyrazolino[2,3-c] [1,2,3] triazole (10b) and cis-4,5-dicarbomethoxy-1,6-diphenyl-3,3a-di(4-methoxyphenyl)-4,5-dihydropyrazolino[2,3-c] [1,2,3] triazole (10c), respectively. The coupling constants between the protons at C₄ and C₅-positions in these adducts are about 10 and 9 Hz, respectively. The calculated dihedral angles in 10b and 10c would correspond to 30° and 35°, respectively. These dihedral angles would suggest that both these adducts have the cis stereochemistry.

Treatment of bisphenylazostilbene (2a) with maleic anhydride gave a 72% yield of the cycloadduct, 1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c] [1,2,3] triazole-4,5-dicarboxylic anhydride (11). The ir spectrum of (11) showed two strong absorption bands at 1850 and 1790 cm⁻¹, characteristic of a five membered dicarboxylic anhydride.

The reactions of the bisphenylazostilbenes, 3a-c with dimethyl fumarate gave the corresponding trans-4,5-dicarbomethoxy-1,6-diphenyl-1,3a-diaryl-4,5-dihydropyrazolino[2,3-c] [1,2,3] triazoles (12a-c), as would be expected in a stereospecific addition. Similar trans-adducts 13 and 14 were obtained in the reaction of 2a with methyl crotonate, and trans-dibenzoyl ethylene, respectively. The coupling constants between the tertiary protons at C₄ and C₅-positions in the adducts 12a-c, 13 and 14 were observed to lie in the range of 5.0-6.5 Hz. The computed dihedral angles in all these cases

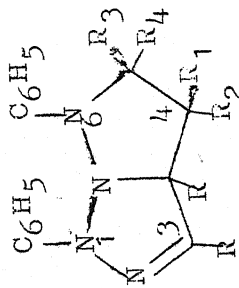
lie in the range of 110° - 125° , thereby indicating that these protons are trans with respect to each other, in each case. Table 3.3 summarises the nmr spectral data of these adducts.

Having established the stereospecificity of these addition products, our next objective was to investigate the regioselectivity in the reactions of 2a-c with unsymmetrically substituted olefinic dipolarophiles. With this view, we have examined the reactions of 1,2-bisphenylazoalkenes, 2a-c with ethyl acrylate and acrylonitrile. Treatment of 2a with ethyl acrylate and acrylonitrile gave the corresponding cycloadducts 15a and 16a, in 76% and 82% yields, respectively. Similar 4,5-dihydropyrazolino[2,3-*c*] [1,2,3] triazoles, 15b and 15c and 16b and 16c were obtained in the reactions of 2b and 2c with ethylacrylate and acrylonitrile, respectively. The structures assigned to all these adducts are supported by their nmr spectral characteristics. The nmr spectrum of 15a (Fig. 3.4) showed a triplet at 0.70δ (3 H) due to the CH_3 protons of the ester ethyl group. The methylene protons at C_5 and the ester methylene protons appeared together as a multiplet at 3.12δ (4 H). The signal due to the tertiary proton at C_4 appeared as a triplet at 3.79δ (1 H). The nmr spectrum of the acrylonitrile adduct 16b (Fig. 3.5) showed a complex multiplet over the range 6.90 - 8.60δ (18 H) due to the aromatic protons and a second multiplet over the range, 3.5 - 4.5δ (3 H), assigned to the methylene and methine protons, at C_5 and C_4 respectively.

Table 3.3

Nmr Spectral Characteristics of Dihydropyrazolino [2,3-c][1,2,3] triazoles

Cycloadduct	Chemical Shift in ppm					
	Phenyl protons (i)	OCH ₃ (C ₄) (iii)	protons (C ₅) (iv)	Other CH ₃ (v)	H(C ₄) (vi)	H(C ₅) (vii)
						J _{4,5} Hz (viii)
						Dihedral Angle (ix)



10a, R=C ₆ H ₅ , R ₁ =R ₃ =H, R ₂ =R ₄ =CO ₂ CH ₃	6.67-8.00	3.07	3.69	3.88	4.41	9.7	32°
10b, R=p-ClC ₆ H ₄ , R ₁ =R ₃ =H, R ₂ =R ₄ =CO ₂ CH ₃	6.76-8.56	3.40	4.05	4.30	4.90	10	30°
10c, R=p-CH ₃ OC ₆ H ₄ , R ₁ =R ₃ =H, R ₂ =R ₄ =CO ₂ CH ₃	6.72-8.63	3.38	3.96	3.76, 4.30	4.94	9	35°

3.80^a

Table 3.3 (...Contd.)

(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
<u>12a</u> , $R=C_6H_5$, $R_1=R_4=H$, $R_2=R_3=CO_2CH_3$	7.05-8.60	3.43			4.20	5.58	3.8
<u>12c</u> , $R=P-CH_3OC_6H_4$, $R_1=R_4=H$	6.60-8.60	3.42	3.54	3.90 ^a	3.88	4.20	3.5
<u>13</u> , $R=C_6H_5$, $R_1=R_4=H$, $R_2=CO_2CH_3$, $R_3=CH_3$	6.60-8.25	3.23		1.36 ^b	3.36	5.00*	4.5

* This signal is a multiplet. Except this, all signals due to protons at C_4 - and C_5 -positions are doublets.

a) Signal due to $P-OCH_3$ of phenyl groups at C_3 - and C_{3a} -positions.

b) Signal due to the CH_3 group at C_5 -position.

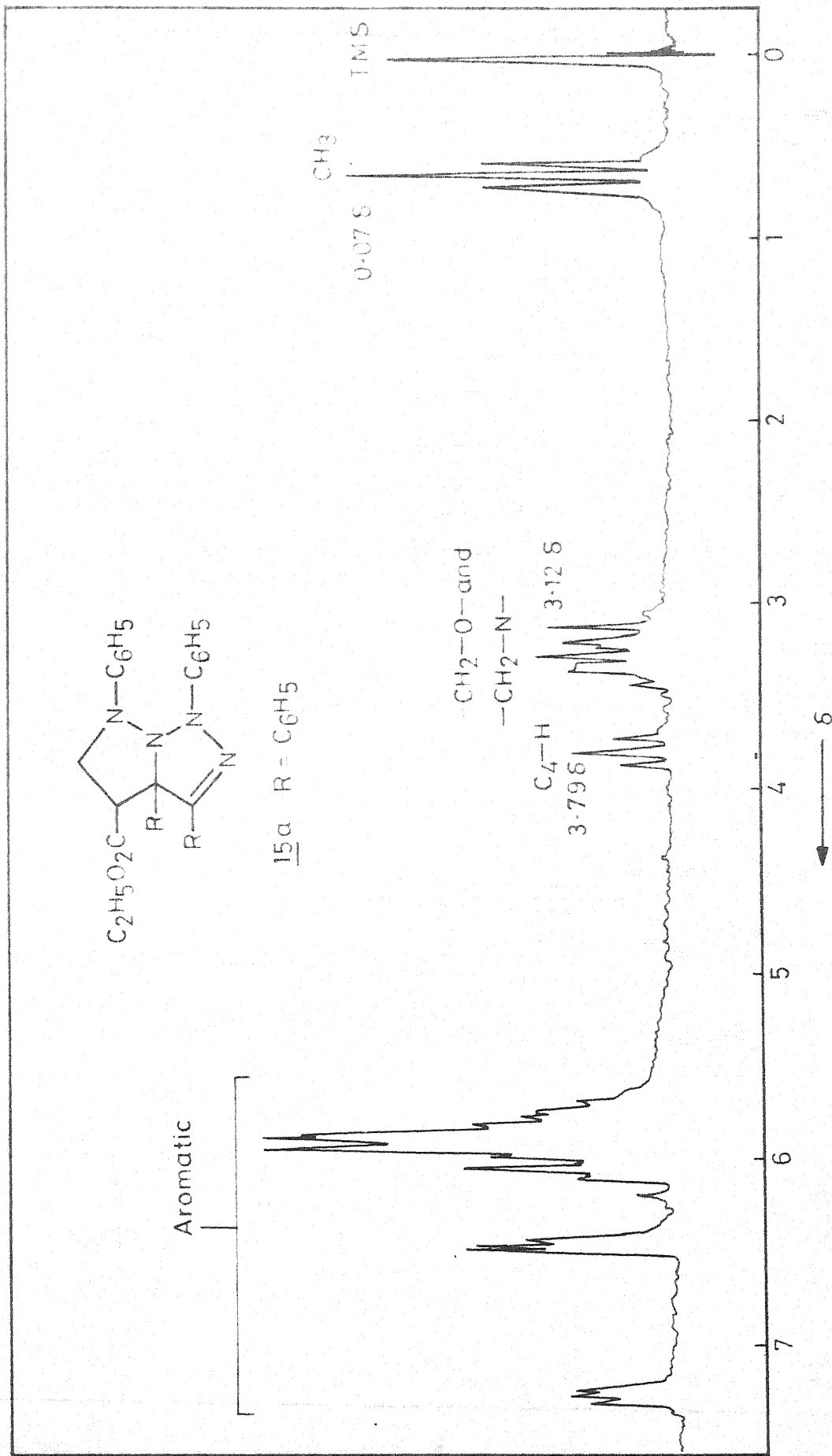
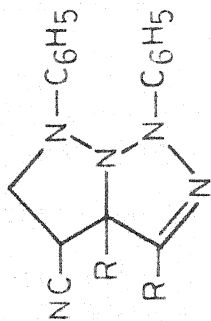
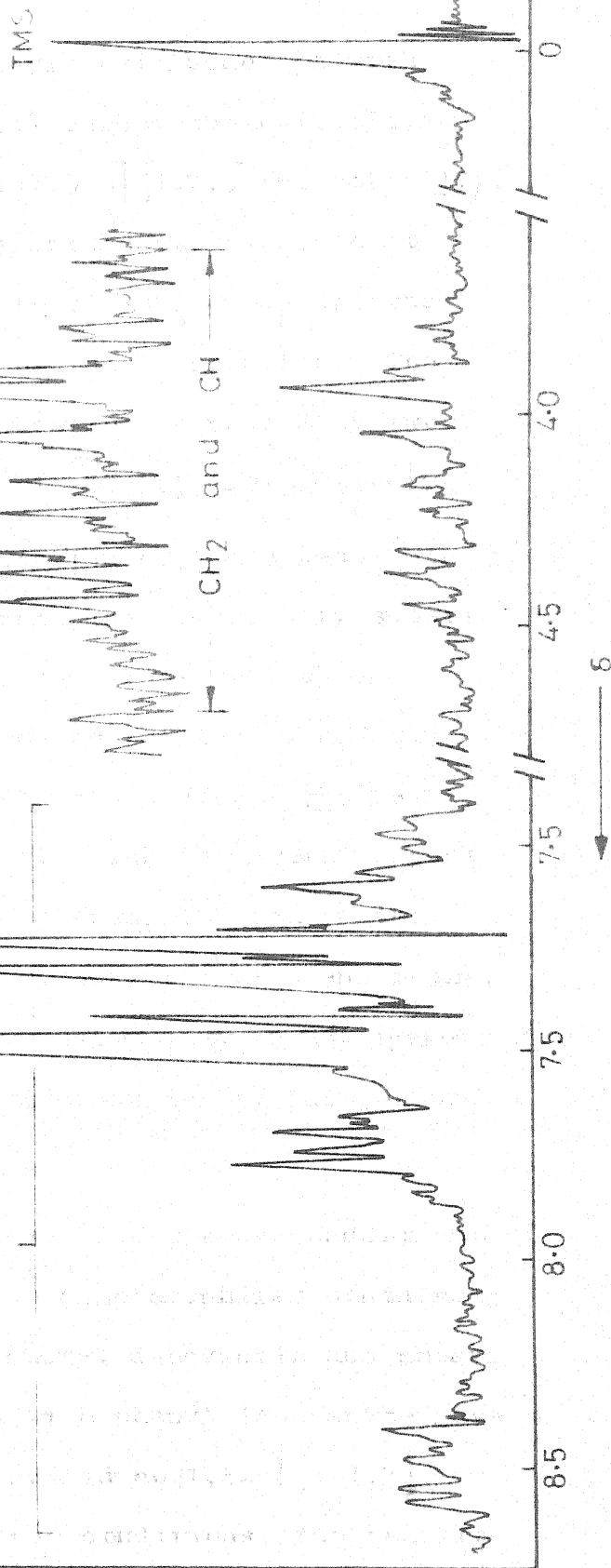


Fig. 3.4 Nmr Spectrum (100 MHz) of 1,3,3a,6-Tetraphenyl-4-carboethoxy-4,5-dihydropyrazolino-[2,3-c][1,2,3]triazole (**15a**).



15b, R = p-Cl-C₆H₄

Aromatic

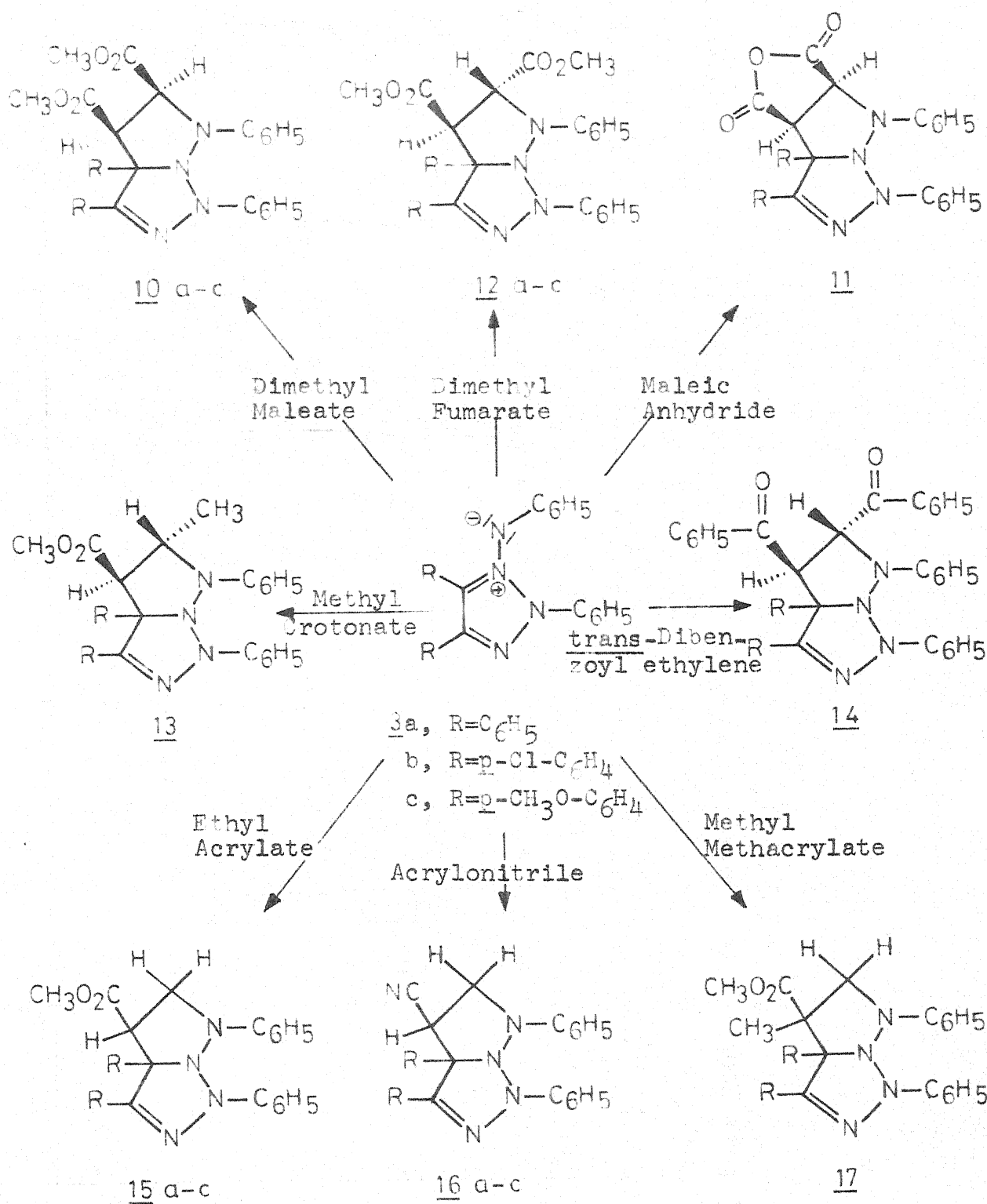


The reaction of the bisphenylazostilbene, 2a with methyl methacrylate gave 4-methyl-4-carbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino [2,3-c] [1,2,3] triazole (17). The nmr spectrum of 17 (Fig. 3.6) showed two singlets at 1.54 δ (3 H) and 3.08 δ (3 H), due to the CH₃ group and the ester methyl group, respectively at the C₄-position. The geminally coupled protons at C₅-positions appeared as two doublets at 3.58 δ and 4.59 δ (J = 11.48 Hz), respectively.

The formation of the adducts 15a-c, 16a-c and 17 in the reactions of 2a-c with different unsymmetrically substituted olefinic dipolarophiles would suggest that these addition reactions proceed in a regioselective manner and that the negative end of the intermediate dipole (3) is getting attached to the carbon atom which is β with respect to the electrophilic ester or cyano group in each of the dipolarophiles like ethyl acrylate, acrylonitrile and methyl methacrylate (Scheme 3.4). Such regioselectivity in 1,3-dipolar cycloaddition reactions has been reported earlier by Huisgen and coworkers in several cases.⁷⁻⁹

In continuation, we have examined the cycloadditions of the bisphenylazostilbenes, 2a-c to dipolarophiles containing cumulative double bonds such as phenyl isocyanate and phenyl isothiocyanate. Treatment of 2a with phenyl isocyanate gave 1,3,3a,4,6-pentaphenyl-1,2,4-triazolidino [1,5-c] [1,2,3] - triazol-5-one (18a). Under similar conditions, the reaction

Scheme 3.4



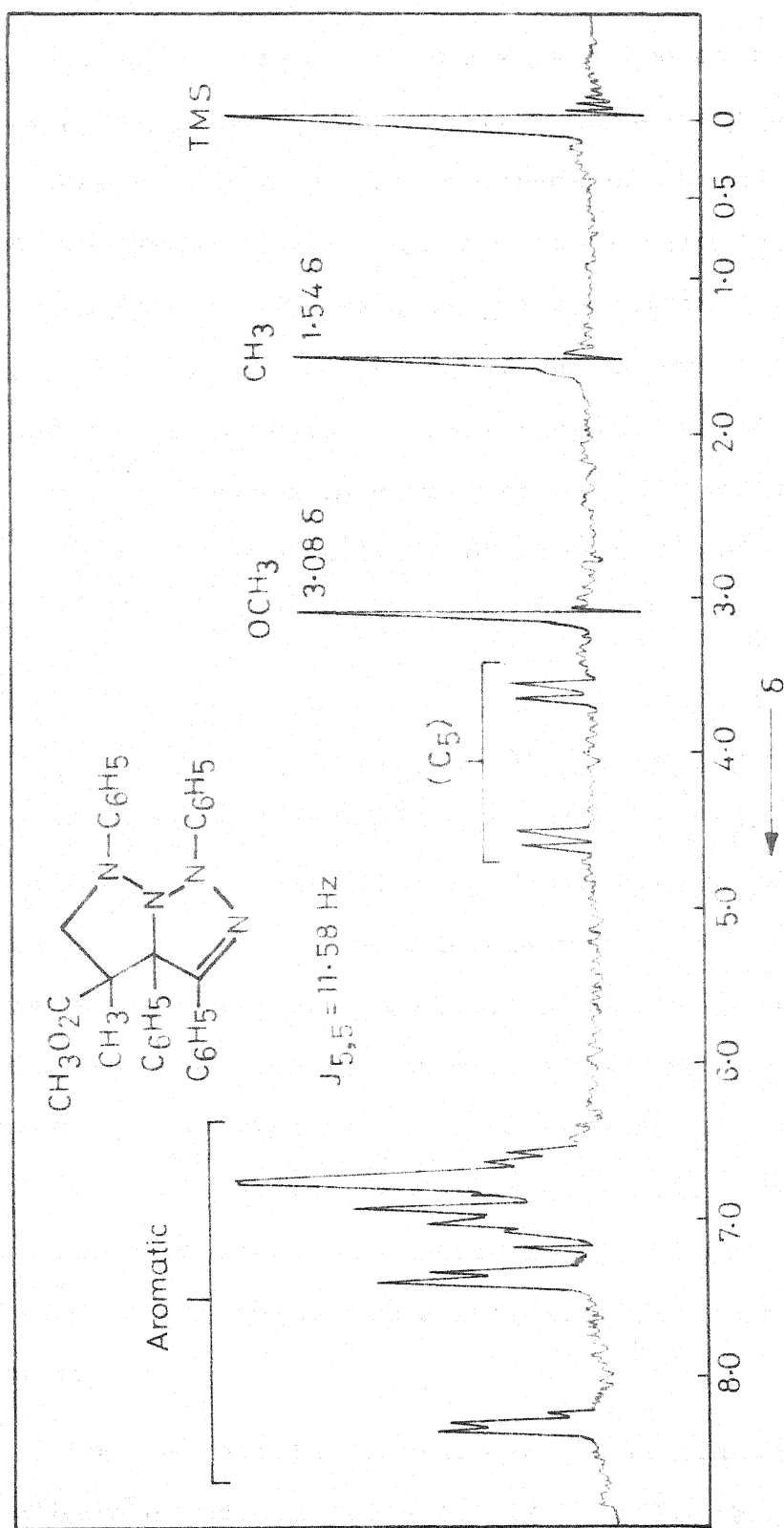


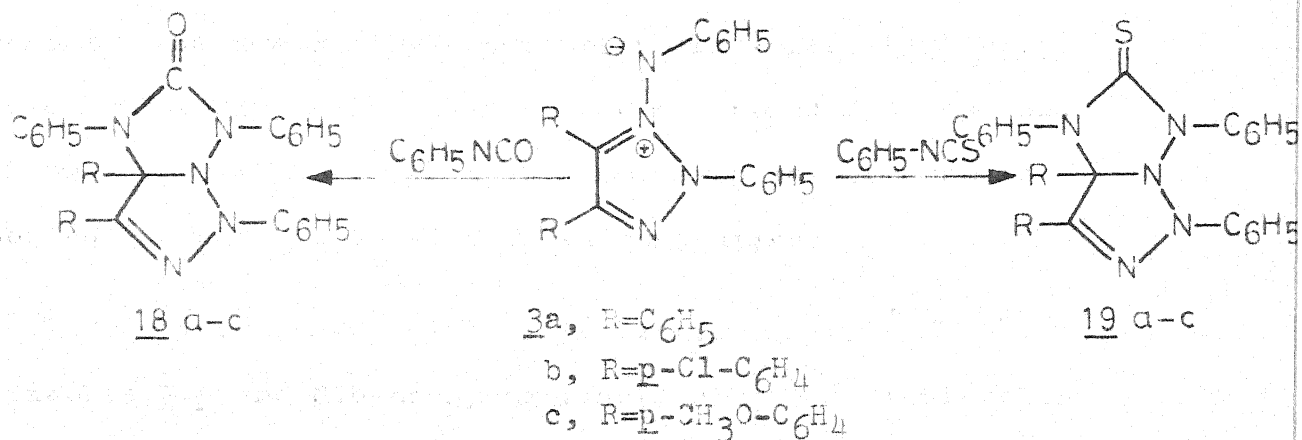
Fig. 3.6 Nmr spectrum (100 MHz) of 1,3,3a,6-Tetraphenyl-1^H-methyl-1^H-carbomethoxy-4,5-dihydropyrazolino [2,3-c] [1,2,3] triazole (17)

of 2a with phenyl isothiocyanate gave the corresponding thione (19a) (Scheme 3.5). Similar adducts 18b-c and 19b-c were obtained in the reactions of 2b and 2c with phenyl isocyanate and phenyl isothiocyanate, respectively. The ir spectra of the adducts 18a-c contained two absorption bands around 1720 and 1590 cm^{-1} , characteristic of a five-membered cyclic ureide, whereas the spectra of the adducts 19a-c showed absorption bands around 1580 and 1490 cm^{-1} , in each case, characteristic of five-membered thioureides¹⁰.

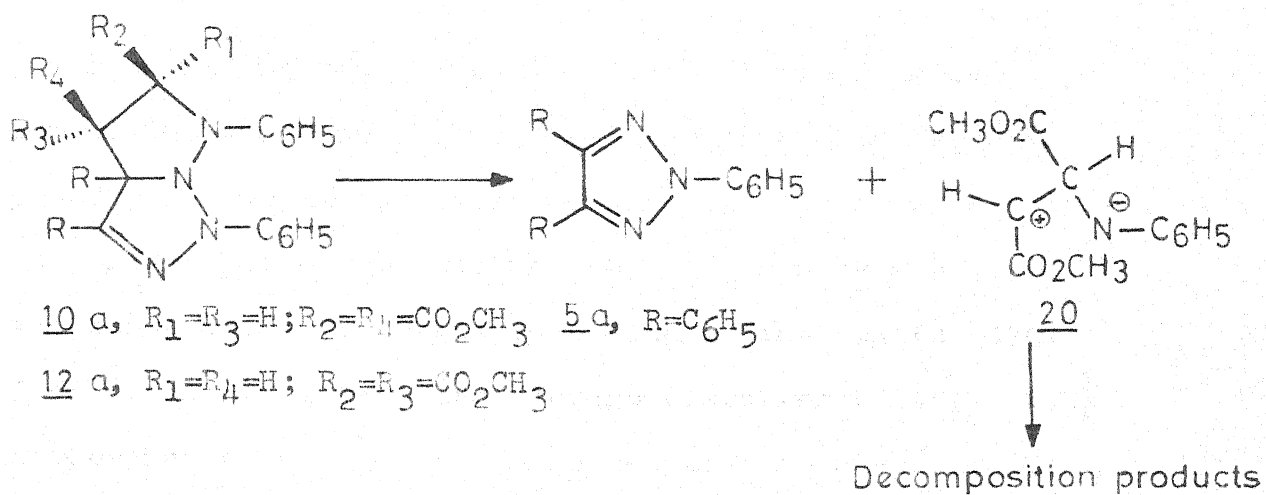
With a view to obtaining some additional chemical evidence for the structure of these adducts, we have examined the thermolysis of two 4,5-dihydropyrazolinotriazoles, 10a and 12a. Heating 10a to around 200° for 15 minutes resulted in the formation of a 87% yield of 2,4,5-triphenyl-1,2,3-triazole (5a). The same triazole was formed in 80% yield in the thermolysis of 12a also. A possible mechanism for the formation of the triazole is given in Scheme 3.6. However, our attempts to trap the mesoionic species 20 or its rearranged products were unsuccessful. It is probable that under our reaction conditions, a species such as 20 would be undergoing further fragmentation to intractable products.

The ultraviolet spectra of pyrazolinotriazoles, 7-9 and dihydropyrazolinotriazoles, 10-17 were characterised by

Scheme 3.5



Scheme 3.6



three absorption maxima. In the case of pyrazolotriazoles, 7-9 which are derived from acetylenic dipolarophiles, the absorption maxima were observed around 250, 305 and 370 nm, whereas in the case of dihydropyrazolotriazoles, (10)-(17), the corresponding maxima were observed around 250, 290 and 330 nm. In Table 3.4, we have summarised the electronic spectral details of some of these derivatives.

The infrared spectra of pyrazolino[2,3-c][1,2,3]-triazoles 7-9 and dihydropyrazolino[2,3-c][1,2,3]triazoles, 10-17 showed a number of characteristic absorption bands. Table 3.5 summarises some of the prominent absorption peaks in these adducts. In the case of the pyrazolino[2,3-c][1,2,3]-triazoles 7a and 8a, for example, several absorption peaks were observed in the region of 1730, 1675, 1570, 1480, 1450, 1245, 775 and 760 cm^{-1} . The 1730 cm^{-1} band was assigned to the ester C=O, stretching vibration.

Cook and Church¹¹ have assigned the bands in the region of 2000-1650 cm^{-1} in the ir spectra of heterocyclic compounds, as due to the overtone and combination frequencies of the out-of-plane C-H bending modes of benzenoid heterocyclic compounds. The bands appearing in the region 1570-1675 cm^{-1} , in pyrazolino and dihydropyrazolino[2,3-c][1,2,3]-triazoles may be due to this mode and/or a combination of this mode with the C=N stretching vibrational modes.

Table 3.4

UV triazole Spectral Characteristics Pyrazolino and Dihydropyrazolino[2,3-c][1,2,3]-triazoles

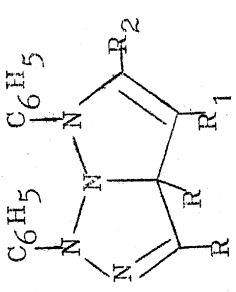
Compound	λ_{\max} nm (ϵ)
	252 (49,000)
	304 (48,500)
	368 (6,500)
7a, $R_1=R_2=CO_2CH_3$	
8a, $R_1=CO_2CH_3$, $R_2=H$	250 (52,000)
9, $R_1=R_2=COC_6H_5$	306 (43,500)
	372 (7,500)
	305 (47,500)
	370 (6,600)

Table 3.4 (...Contd.)

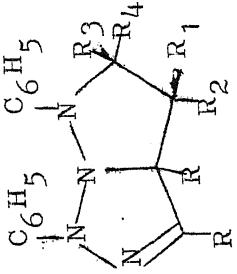
Compound	λ_{\max} nm (ϵ)
	
<u>10a</u> , $R_1=R_3=H$, $R_2=R_4=CO_2CH_3$	246 (58,000) 288 (14,000) 332 (5,600)
<u>12a</u> , $R_1=R_4=H$, $R_2=R_3=CO_2CH_3$	246 (53,000) 290 (13,600) 332 (6,800)
<u>13</u> , $R_1=R_4=H$, $R_2=CO_2CH_3$, $R_3=CH_3$	260 (44,000) 298 (12,000) 334 (5,600)
<u>14</u> , $R_1=R_3=H$, $R_2=R_4=COC_6H_5$	244 (66,000) 291 (14,000) 330 (2,100)
<u>15a</u> , $R_1=R_3=R_4=H$, $R_2=CO_2C_2H_5$	256 (40,000) 298 (10,300) 328 (4,000)
<u>16a</u> , $R_1=R_3=R_4=H$, $R_2=CN$	250 (28,200) 288 (6,700) 328 (4,000)
<u>17</u> , $R_1=CH_3$, $R_2=CO_2CH_3$, $R_3=R_4=H$	258 (45,000) 296 (11,000) 328 (4,500)

Table 3.5

Infrared Spectral Characteristics of Pyrazolino[2,3-c] [1,2,3] triazoles Dihydropyrazolino-[2,3-c] [1,2,3] triazoles (cm^{-1}) and 1,2,4-Triazolino[1,5-c] [1,2,3] triazol-5-ones and the

Corresponding Thiones

Cyclo- adduct	C=O Stretching	C-H Bending and/or C=N Stretching	Ring Bending	In-plane, CH-Deformation and Ring Breathing Modes	Out-of-plane CH-Deformations
(i)	(ii)	(iii)	(iv)	(v)	(vi)
<u>7a</u>	1725	1675	1570 1480	1450 1275	775 760
<u>7b</u>	1770, 1710	1490	1490 1410	1340 1150 1000	780 750
<u>7c</u>	1760, 1710	1600	1500 1420	1330 1120 1040	780 730
<u>8a</u>	1730	1670	1575 1480	1460 1240	775 755
<u>8b</u>	1730	1590	1500	1300 1100 1020	770 750
<u>8c</u>	1730	1610	1510	1350 1120 1040	770 750
<u>9</u>	1675	1575	1490 1420	1310 1160 1010	770 730
<u>10a</u>	1730	1590	1490 1455	1320 1200 1155	770 750
<u>10b</u>	1725	1595	1490 1460	1330 1190 1150	770 755
<u>10c</u>	1730	1600	1500 1450	1400 1200 1030	760 750
<u>11</u>	1850, 1790 ^a	1565	1490 1450	1325 1190 1150	770 755

Table 3.5 (...Contd.)

(i)	(ii)	(iii)	(iv)	(v)	(vi)					
<u>12a</u>	1730	1590	1475	1450	1100	1030	775	750		
<u>12b</u>	1730	1585	1480	1450	1330	1180	1050	970	770	755
<u>12c</u>	1710	1590	1495	1450	1390	1200	1050	985	770	750
<u>13</u>	1720	1570	1475	1440	1360	1205	1025		785, 765	730
<u>14</u>	1690	1500	1440				990			
<u>15a</u>	1720	1600	1490	1460		1110	950		770	750
<u>15b</u>	1720	1590	1490	1460	1390	1200	1050	980	780	740
<u>15c</u>	1710	1580	1490	1475	1395	1190	1040	945	780	750
<u>16a</u>	2210 ^b	1535	1475	1450			1045	975	770	
<u>16b</u>	2220 ^b	1585	1480	1450	1360	1160	1040	980	770	740
<u>16c</u>	2210 ^b	1585	1480	1440	1350	1170	1040	980	780	755
<u>17</u>	1725	1580	1490	1430	1360	1160	1035	985	760	755
<u>18a</u>	1720, 1590 ^c		1475	1450	1390	1120	1020	975	775	740
<u>18b</u>	1710, 1590 ^c		1470	1450	1400	1130	1030	970	775	740
<u>18c</u>	1720, 1595 ^c		1480	1445	1395	1125	1020	980	780	745

Table 3.5 (...Contd.)

(i)	(ii)	(iii)	(iv)	(v)	(vi)
<u>35</u>	1680, 1590 ^c	1470	1450	1390	1130
<u>19a</u>	1574, 1475 ^d	1470	1440	1380	1120
<u>19b</u>	1590, 1485 ^d	1465	1435	1370	1125
<u>19c</u>	1605, 1510 ^d	1470	1435	1360	1130
<u>36</u>	1600, 1510 ^d	1480	1440	1370	1120

- a) C=O of five-membered anhydride,
b) C≡N stretching vibration,
c) C=O of five-membered ureide,
d) C=S of five-membered thioureide.

Ring stretching vibrations in five-membered rings appear as three bands around 1590, 1490 and 1400 cm^{-1} , respectively¹² and the corresponding values for 1,2,3-triazoles are 1520, 1450, and 1400 cm^{-1} , respectively.¹³ On the other hand, in a condensed ring system like indole,¹⁴ these bands appear around 1460, 1420 and 1350 cm^{-1} . For quinazolines,¹⁵ the corresponding band positions are in the range 1628-1612, 1584-1566 and 1517-1478 cm^{-1} , respectively. In the ir spectra of pyrazolino and dihydropyrazolino[2,3-c][1,2,3] triazoles, three bands were observed in the region of 1575-1475, 1480-1420 and 1450-1310 cm^{-1} . These bands are likely to be due to the ring bending vibrations of the condensed pyrazolino and dihydropyrazolino[2,3-c][1,2,3]-triazole systems. A series of characteristic bands appearing in the range of 1245-950 cm^{-1} have been assigned to the in-plane C-H deformation and ring-breathing modes. On the other hand, the bands in the range 785-730 cm^{-1} may be due to the C-H, out-of-plane deformations. These assignments are consistent with band positions reported for a number of heterocyclic compounds.^{7,9}

Having established the stereospecificity and regioselectivity of the addition of dipolarophiles to the bisphenylazostilbenes 2a-c, we then attempted to investigate the kinetics of some of these addition reactions. It has

been generally recognised that cycloadditions and other concerted processes, which involve ordered transition states proceed with relatively low energies of activation. The entropy of activation of such processes are large and negative in sign as is to be expected when the transition states are more ordered, than the starting reactants.

The anhydro iminotriazolium hydroxide 3a, probably in equilibrium with the bisphenylazostilbene (2a) has a characteristic absorption maximum at 404 nm ($\epsilon \sim 12000$) whereas, neither the dipolarophiles nor the corresponding cycloadducts show any absorption in this region. Hence we could conveniently follow the progress of the addition reaction, spectrophotometrically, by measuring the rate of decrease in intensity of this absorption maximum. In each case, a known excess (800-1000 times) of the dipolarophile was taken. Plots of the logarithm of optical density against time gave very good straight lines. The pseudo-first order rate constants were determined from the slopes of these lines and the second order rate constants were computed from these results. The values of energy and entropy of activation were determined in the usual way. Table 3.6 summarises the kinetic data of some of these addition reactions.

As is evident from Table 3.6, these reactions proceed with relatively low activation energies and rather large

Table 3.6

Kinetic Data for the Reaction of Bisphenylazostilbene (2a)
with Different Dipolarophiles*

Dipolarophile	Rate constant at 30°C (litre mol ⁻¹ sec ⁻¹)	$\Delta E^\ddagger(\pm 1)$ kcal mol ⁻¹	$\Delta S^\ddagger(\pm 2)$ eu
1) Dimethyl acetylene dicarboxylate	2.16×10^{-1}	9.0	-34
2) Methyl propiolate	2.692×10^{-2}	5.6	-49
3) Dimethyl maleate	1.485×10^{-3}	9.5	-36
4) Dimethyl fumarate	2.59×10^{-5}	8.0	-38
5) Ethyl acrylate	1.521×10^{-4}	13.5	-34
6) Methyl methacrylate	3.72×10^{-5}	11.0	-37
7) Methyl crotonate	7.25×10^{-6}	10.3	-34
8) Acrylonitrile	6.026×10^{-4}	10.0	-42
9) Phenyl isocyanate	4.21×10^{-4}	14.5	-33
10) Phenyl isothiocyanate	8.913×10^{-4}	13.4	-26

*For the same dipolarophile, measurements at different temperatures were made starting with the same initial concentrations so that log OD vs time plots intersected at zero time. This was used as a check for the accuracy of measurement and also the invariance of the mechanism of the reaction in the temperature range in which measurements were made.

negative values of entropies of activation, as is to be expected of concerted processes with cyclic transition states. The relative rates of addition of various dipolarophiles to 2a by and large, followed a parallel trend as the rates of addition of these dipolarophiles to analogous dipolar species.^{16,17} Olefinic substrates with a trans-geometry have been reported to react faster than their cis-isomers in 1,3-dipolar cycloaddition reactions.¹⁶ However, in the case of 2a we find that the cis-isomer reacts about 60 times faster than the trans-isomer. Molecular models show that the transition state leading to the formation of the trans-adduct is more crowded than the cis-adduct. It is probable that the more stringent steric requirements of 3a as compared to other dipolar species is responsible for the reverse trend observed in these cases.

In the case of substituted imino-triazolium derivatives 3b and 3c also we have observed that cis-dipolarophiles react faster than their trans-isomers. In Table 3.7, we have summarised the rate constants of some of these reactions, illustrating such a trend in these cycloadditions.

Having established that various bisphenylazostilbenes exist in valence tautomeric equilibrium with the mesoionic anhydro 1-phenylimino-2-phenyl-4,5-diaryl-1,2,3-triazolium hydroxides, and having shown that in this latter form they

Table 3.7

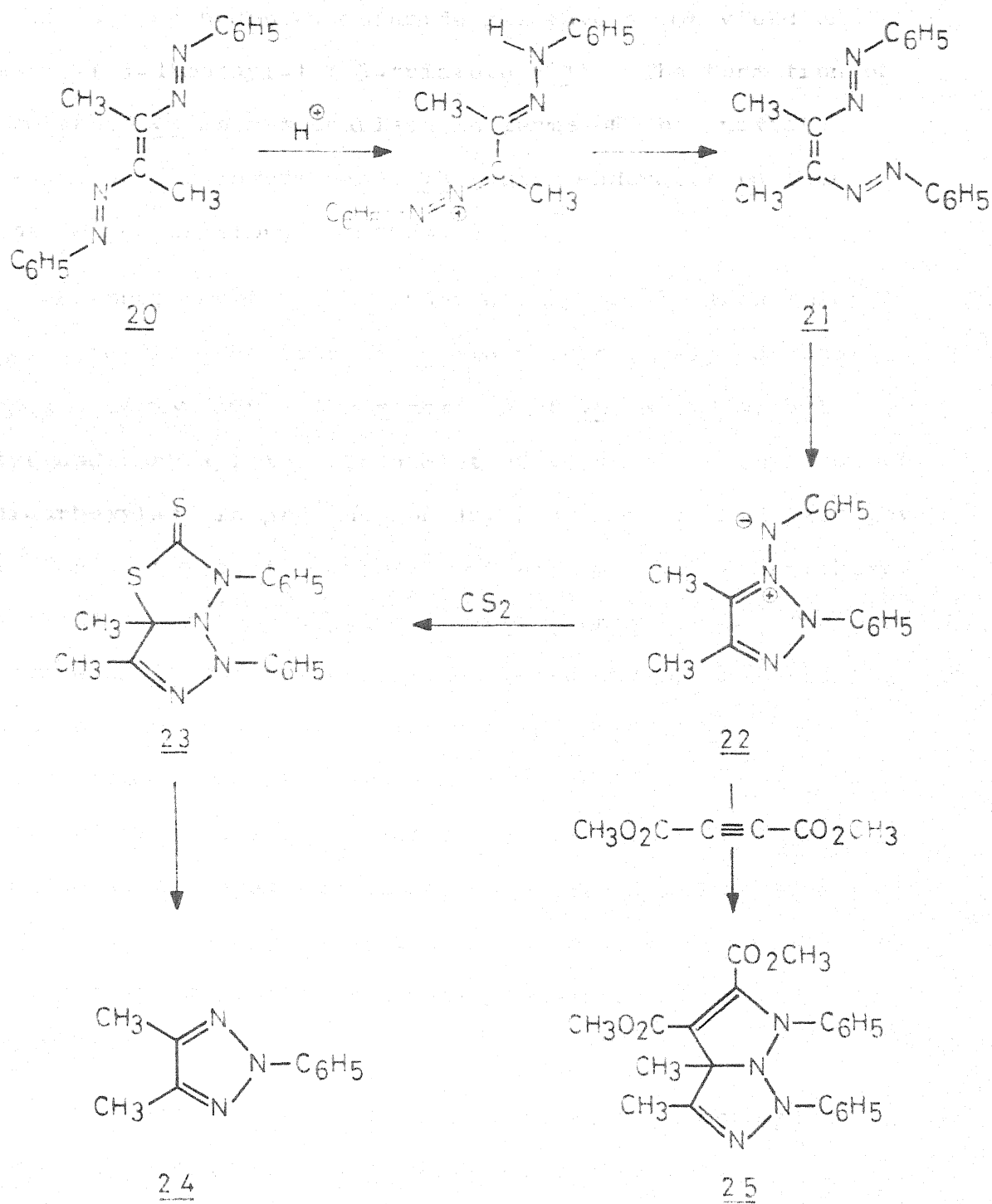
Kinetics of Cycloaddition of 1,2-Bisphenylazoalkenes (2a-c) to Acetylenic and Olefinic Dipolarophiles

Bisphenylazoalkene	Rate constant at 35°C litre mol ⁻¹ sec ⁻¹		
	Dimethyl acetylene dicarboxylate	Dimethyl maleate	Dimethyl fumarate
Bisphenylazostilbene (<u>2a</u>)	2.661×10^{-1}	1.56×10^{-3}	2.68×10^{-5}
1,2-Bisphenylazo-1,2-di-(4-chlorophenyl)ethylene (<u>2b</u>)	6.487×10^{-2}	1.217×10^{-4}	5.277×10^{-6}
1,2-Bisphenylazo-1,2-di-(4-methoxyphenyl)ethylene (<u>2c</u>)	5.309×10^{-2}	1.922×10^{-4}	3.007×10^{-6}

undergo 1,3-dipolar cycloaddition reactions with acetylenic and olefinic dipolarophiles, we then wanted to see how this equilibrium itself is affected by a possible alteration in the stereochemistry about the carbon-carbon double bond. It is reasonable to assume that such valence isomerisation will be very facile if the two phenylazo groups are cis with respect to each other. Although it is possible to visualise a thermal cis-trans isomerisation as shown in Scheme 3.7, we felt that the likelihood of such a process occurring is rather negligible in the absence of any catalysis by acids. To prove this point we chose to investigate the valence isomerism of two bisphenylazoalkenes, namely, 2,3-bisphenylazo-2-butene (20) and 1,2-bisphenylazocyclohexene (26).

In Chapter 2, we have reported that 20 failed to undergo thermolysis or photolysis in the absence of hydrogen chloride. On the other hand, it was shown that in presence of catalytic amounts of acids, 20 undergoes photolysis to yield 2-phenyl-4,5-dimethyl-1,2,3-triazole. It has been suggested that under acid-catalysis, the isomerization of 20 to its cis-isomer 21 is feasible and that the formation of the triazole can be rationalised in terms of an intermediate like 22 (Scheme 3.7). With a view to confirming whether the azomethineimine intermediate 22 is actually involved in such transformations, we have examined the reaction of 20 in presence of dry hydrogen chloride gas with

Scheme 3.7



a suitable dipolarophile like carbon disulphide. Treatment of a mixture of 20 with excess of carbon disulphide in presence of dry hydrogen chloride gas gave a 60% yield of 2-phenyl-4,5-dimethyl-1,2,3-triazole (24). The formation of the triazole 24 is rationalised in terms of the initial formation of the intermediate 23, which undergoes further fragmentation as shown in Scheme 3.7.

Further proof of the intermediacy of the azomethine-imine 22 in the reactions of 20 under acid-catalysed conditions was derived from the reactions of 20 with dimethyl acetylenedicarboxylate. Treatment of 20 with dimethyl acetylenedicarboxylate in presence of dry hydrogen chloride gas gave a 62% yield of 2,6-diphenyl-3,3a-dimethyl-4,5-dicarbomethoxypyrazolino[2,3-c][1,2,3] triazole (25) (Scheme 3.7). The structure of 25 was established on the basis of analytical results and spectral data. The nmr spectrum of 25, for example, showed two singlets at 1.55δ (3 H) and 1.90δ (3 H), due to methyl groups at C₃ and C_{3a}-positions, respectively. In addition, the spectrum showed two separate singlets at 3.75δ (3 H) and 3.85δ (3 H) due to ester methyl groups. The phenyl protons appeared as a multiplet around 7.50δ (10 H) (Fig. 3.7).

In continuation of our studies, we have attempted to study the reactions of 20 with other dipolarophiles like

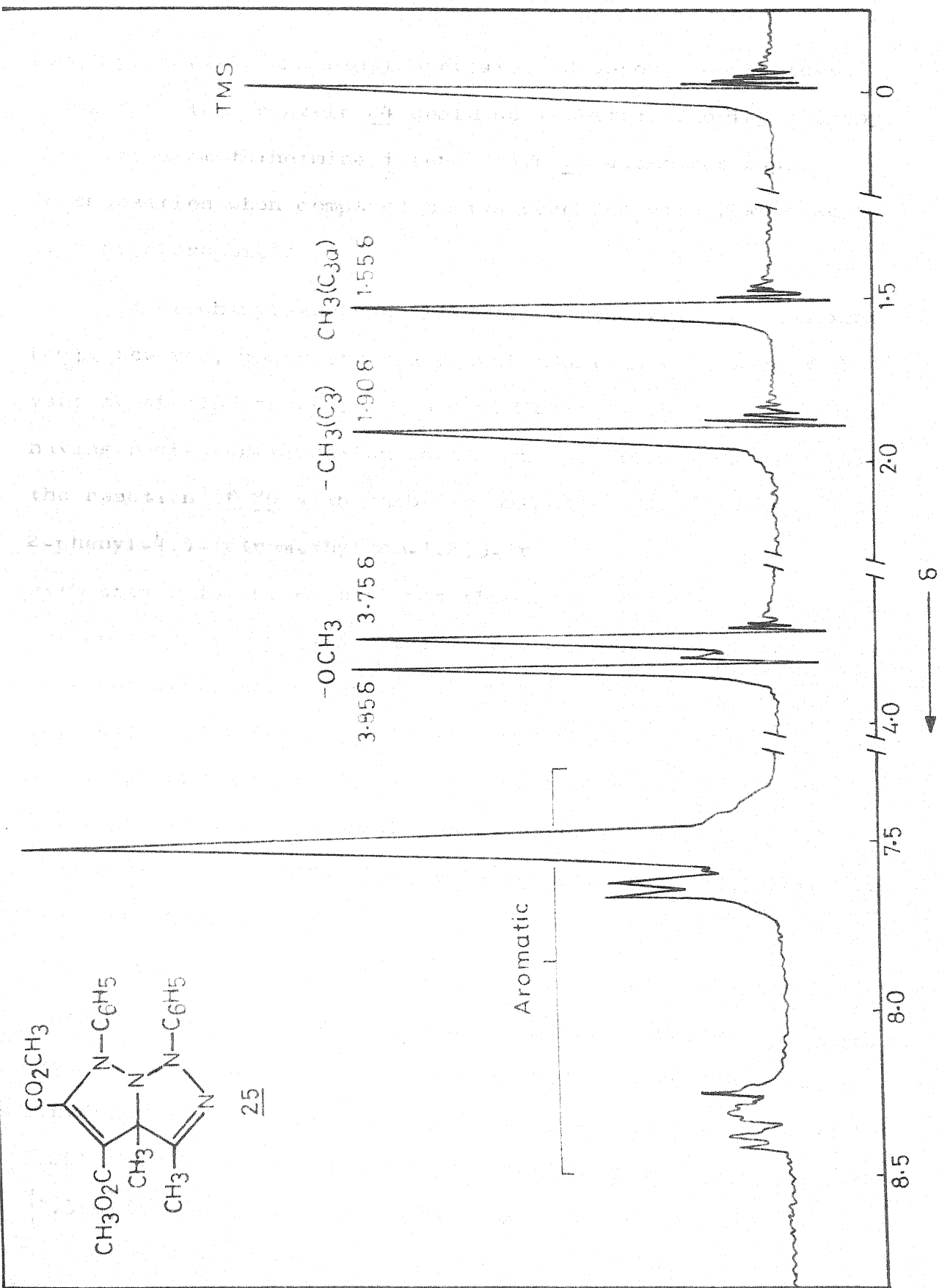


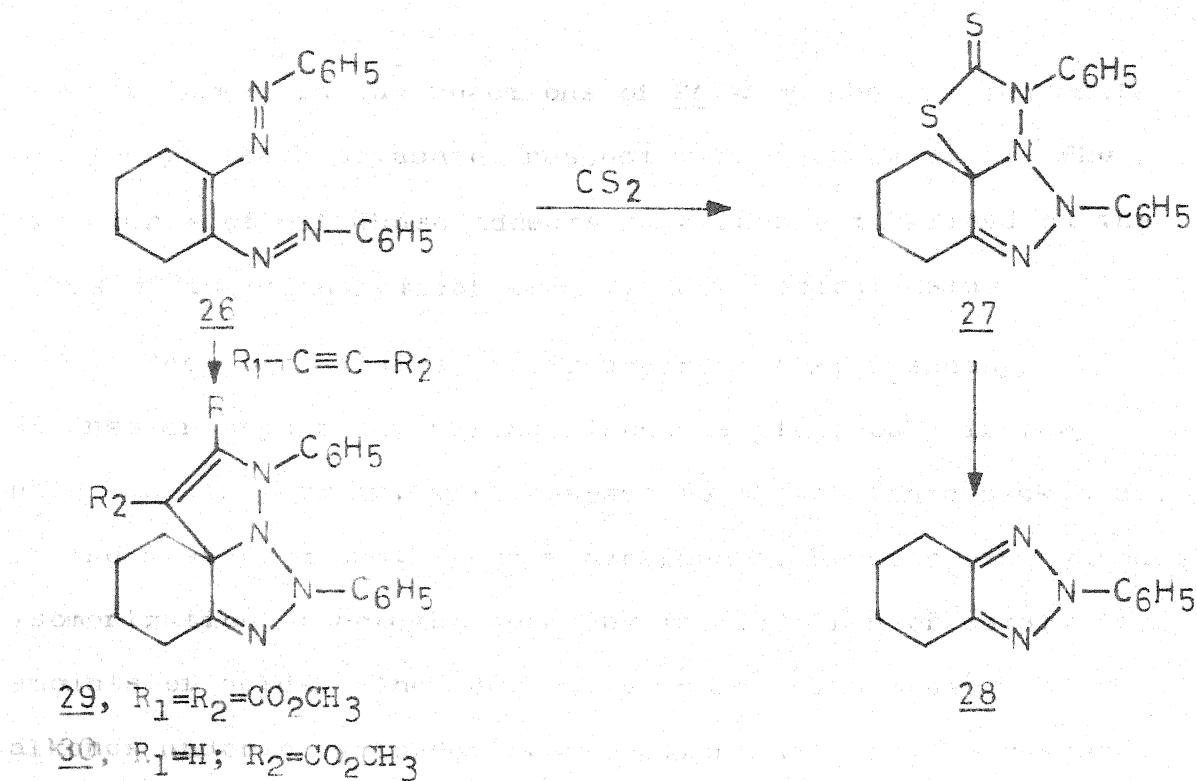
Fig. 3.7 Nmr Spectrum (60 MHz) of 1,6-Diphenyl-3,3a-dimethyl-4,5-dicarbomethoxy-

dimethyl maleate and ethyl acrylate. However, in all these cases only the triazole 24 could be isolated, showing thereby that the azomethineimine intermediate 22 undergoes rapid decomposition when compared to its reaction with less reactive dipolarophiles.

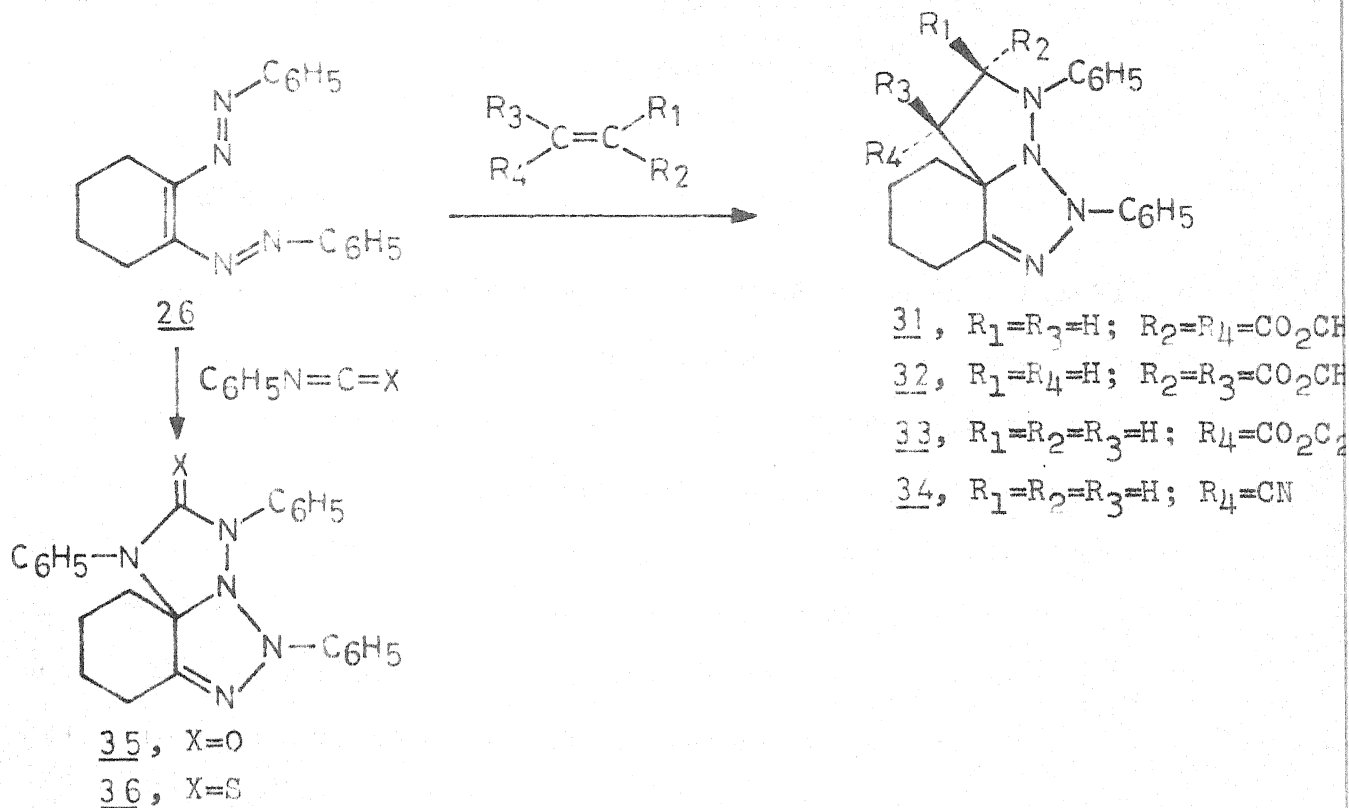
A bisphenylazoalkene like 1,2-bisphenylazo cyclohexene (26), however, underwent ready cycloaddition reactions with a variety of dipolarophiles, as would be expected of a compound having a cis-configuration across the olefinic linkage. Thus, the reaction of 26 with carbon disulphide, for example, gave 2-phenyl-4,5-tetramethylene-1,2,3-triazole (28), together with phenyl isothiocyanate and elemental sulphur (Scheme 3.8). The reaction of 26 with dimethyl acetylenedicarboxylate, gave 1,6-diphenyl-3,3a-tetramethylene-4,5-dicarbomethoxypyrazolino-[2,3-c][1,2,3] triazole (29), in a 60% yield. The reaction with methyl propiolate, on the other hand gave a 43% yield of 1,6-diphenyl 3,3a-tetramethylene-4-carbomethoxypyrazolino-[2,3-c][1,2,3] triazole (30), arising through a regioselective reaction (Scheme 3.8).

The reaction of 26 with olefinic dipolarophiles dimethyl maleate, dimethyl fumarate, ethyl acrylate and acrylonitrile, gave the corresponding 1,6-diphenyl-3,3a-tetramethylene-4,5-dihydropyrazolino[2,3-c][1,2,3] triazoles, 31-34 in good yields. Similarly, 1,4,6-triphenyl-3,3a-tetramethylene-1,2,4-triazolidino-[1,5-c][1,2,3] triazol-5-one (35) and the corresponding thione

Scheme 3-8



Scheme 3-9



36 were formed in the reactions of 26 with phenyl isocyanate and phenyl isothiocyanate, respectively (Scheme 3.9). The structures of all these adducts have been established on the basis of their analytical results and spectral data.

From our studies, it is apparent that bisphenylazoalkenes undergo ready valence isomerisation, only if they have the cis-geometry with respect to the olefinic back-bone. In the case of trans-bisphenylazoalkenes, however, the valence isomerization is brought about by the addition of catalytic amounts of acids. The conditions under which these bisazoalkenes undergo cycloaddition reactions will in themselves could give an indirect indication concerning the geometry of these compounds. Correlation between the structures of bisazoalkenes and the parent 1,2-diketone bisphenyl hydrazones may also become possible through such studies.

3.3 EXPERIMENTAL

All melting points are uncorrected and were determined on a Melt-Temp, melting point apparatus. The ir spectra were recorded on a Perkin Elmer, Model 137 infrared spectrometer and electronic spectra on a Beckmann DB spectrophotometer. The ir and uv spectral data are presented in tabular forms in section 3.2. Nmr traces were recorded either on a Varian A60D NMR spectrometer or a Varian HR100 NMR Spectrometer, using tetramethylsilane as the internal standard.

Starting Materials

1,2-Bisphenylazostilbene (2a), mp 179°, 1,2-bisphenylazodi(4-chlorophenyl)ethylene (2b), mp 205°, 1,2-bisphenylazodi(4-methoxyphenyl)ethylene (2c), mp 175°, 2,3-bisphenylazo-2-butene, (20), mp 149°, were prepared by the oxidation of the corresponding 1,2-diketone bisphenylhydrazones, employing nickel peroxide as per a reported procedure.³

Dimethyl acetylenedicarboxylate, bp 100° (5mm), dibenzoylacetylene, mp 110°, dimethyl fumarate, mp 104°, dimethyl maleate, bp 196°, methyl crotonate, bp 126°, phenyl isocyanate, bp 159° and phenyl isothiocyanate, bp 99° (15 mm) were prepared by reported procedures. Commercially available samples of methyl propiolate, maleic anhydride, trans-dibenzoylthylene, acrylonitrile, ethyl acrylate, methyl methacrylate and carbon disulphide were purified either by distillation or fractional crystallisation before use. 1,2-Bisphenylazocyclohexene (26), mp 127-128° was prepared as per the procedure described in Chapter 2.

Addition of Carbon Disulphide to 1,2-Bisphenylazoalkenes (2a-c and 26)

In a typical experiment 1 mmol of the bisphenylazoalkene and 2 ml of carbon disulphide was left at room temperature for 20 minutes. The unchanged carbon disulphide was removed under reduced pressure and the residue was treated

Starting Materials

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Addition of Carbon Disulphide to 1,2-Bisphenylazoalkenes (2a-c and 26)

In a typical experiment 1 mmol of the bisphenylazoalkene and 2 ml of carbon disulphide was left at room temperature for 20 minutes. The unchanged carbon disulphide was removed under reduced pressure and the residue was treated

with a mixture (1:1) of petroleum ether (bp 60-80°) and benzene. The insoluble residue was identified as elemental sulphur. Removal of the solvent from the benzene petroleum ether soluble portion and recrystallisation of the residue, in each case, gave the corresponding 2-phenyl-4,5-disubstituted triazole. Removal of the solvent from the mother liquor and distillation of the residue gave phenyl isothiocyanate, identified through its ir spectrum. Thus, the reaction of 1,2-bisphenylazostilbene (2a) with carbon disulphide gave 83% yield of elemental sulphur, 66% yield of phenyl isothiocyanate and 93% yield of 2,4,5-triphenyl-1,2,3-triazole, mp 124° (mmp).³

Similarly, 1,2-bisphenylazo(4,4'-dichlorophenyl)-ethylene (2b) with carbon disulphide gave elemental sulphur (40%), phenyl isothiocyanate (54%) and 2-phenyl-4,5-di-(4-chlorophenyl)-1,2,3-triazole (86%), mp 155° (mmp).³

In the reaction of 1,2-bisphenylazo(4,4'-dimethoxyphenyl)ethylene (2c) with carbon sulphide, a 36% yield of sulphur, 50% yield of phenyl isothiocyanate and 85% yield of 2-phenyl-4,5-di(4-methoxyphenyl)-1,2,3-triazole, mp 133° (mmp)³ were obtained.

The reaction of 1,2-bisphenylazocyclohexene (26) gave with carbon disulphide, likewise, elemental sulphur (40%), phenyl isothiocyanate (45%) and 2-phenyl-4,5-tetramethylene-1,2,3-triazole, mp 90° (mmp).

Reaction of Acetylenic Dipolarophiles with 1,2-Bisphenyl
azoalkenes (2a-c and 26)

In a representative run, an equimolar mixture of the bisphenylazoalkene and the acetylenic dipolarophile (1 ~~mmol~~ mol each) was taken in 2 ml acetone and the solution was refluxed for 30 minutes. The solid product that separated out on concentration of the reaction mixture was recrystallised from a mixture (1:1) of benzene and petroleum ether (bp 60-80°), to give the corresponding pyrazolino [2,3-c] [1,2,3] triazole, in each case.

Reaction of 1,2-bisphenylazostilbene (2a) with dimethyl acetylenedicarboxylate gave a 83% yield of 1,3,3a,6-tetraphenyl-4,5-dicarbomethoxypyrazolino [2,3-c] [1,2,3] triazole (7a), mp 184°.

Anal. Calcd for $C_{32}H_{26}N_4O_4$: C, 72.66; H, 4.88, N, 10.35.
Found: C, 72.45; H, 4.99; N, 10.02.

Similarly, the reaction of 2a with methyl propiolate gave a 78% yield of 1,3,3a,6-tetraphenyl-4-carbomethoxypyrazolino [2,3-c] [1,2,3] triazole (8a), mp 196°.

Anal. Calcd for $C_{30}H_{24}N_4O_2$: C, 76.28; H, 5.08; N, 11.87.
Found: C, 76.32; H, 5.10, N, 11.79.

On the other hand, the reaction of 2a with dibenzoylacetylene gave a 64% yield of 1,3,3a,6-tetraphenyl 4,5-dibenzoylpyrazolino [2,3-c] [1,2,3] triazole (9), mp 193°.

Anal. Calcd for $C_{32}H_{28}N_4O_4$: C, 72.18; H, 5.26; N, 10.53.
Found: C, 72.21; H, 5.43; N, 10.63.

Reaction of 1,2-bisphenylazocyclohexene (26) with dimethyl acetylenedicarboxylate gave a 60% yield of 1,6-diphenyl-3,3a-tetramethylene-4,5-dicarbomethoxypyrazolino[2,3-c][1,2,3]-triazole (29), mp 161°.

Anal. Calcd for $C_{24}H_{24}N_4O_4$: C, 66.67; H, 5.56; N, 12.96. Found: C, 66.78; H, 5.75; N, 13.15.

The ir spectrum of 29 showed peaks at 2910, 1730 and 1690 cm^{-1} (C=O), 1510, 1410, 1330, 1140, 1030, 970, 775 and 740 cm^{-1} .

Treatment of 26 with methyl propiolate gave a 43% yield of 1,6-diphenyl-3,3a-tetramethylene-4-carbomethoxy pyrazolino[2,3-c][1,2,3]triazole (30), mp 155°.

Anal. Calcd for $C_{22}H_{22}N_4O_2$: C, 70.59; H, 5.88; N, 14.97. Found: C, 70.31; H, 5.52; N, 15.05.

The ir spectrum of 30 showed bands at 2905, 1690 (C=O), 1550, 1500, 1390, 1350, 1145, 1025, 760 and 735 cm^{-1} .

The nmr spectral details of the pyrazolinotriazoles, 7a-c, 8b-c, 29 and 30 are shown in Table 3.2. The uv and ir spectral data have been reported earlier under Tables 3.4 and 3.5, respectively.

Reaction of 1,2-Bisphenylazoalkenes (2a-c and 26) with Olefinic Dipolarophiles

In a typical experiment, 1 mmol of the bisphenylazoalkene and 5 mmol of the dipolarophile in 3 ml of ethyl acetate was refluxed for 5 hr. The solvent was then removed under reduced pressure and the residue was chromatographed over alumina. Elution with petroleum ether (bp, 60-80°) gave the unchanged dipolarophile. Continued elution with benzene furnished the cycloadducts, whereas, still further elution with ethyl acetate gave the unchanged starting bisazoalkene.

Reactions of 1,2-Bisphenylazoalkenes (2a-c and 26) with Dimethyl Maleate

Reaction of 1,2-bisphenylazostilbene (2a) with dimethyl maleate gave a 79% yield of cis 4,5-dicarbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c] [1,2,3]-triazole (10a), mp 200°.

Anal. Calcd for $C_{32}H_{28}N_4O_4$: C, 72.15; H, 5.26; N, 10.53. Found: C, 72.13; H, 5.00; N, 10.02.

Treatment of 1,2-bisphenylazo(4,4'-dichlorophenyl)-ethylene (2b) with dimethyl maleate gave a 59% yield of the corresponding dihydropyrazolino[2,3-c] [1,2,3] triazole (10b), mp 210°.

Anal. Calcd for $C_{32}H_{26}N_4O_4Cl_2$: C, 64.00; H, 4.33; N, 9.33. Found: C, 64.25; H, 4.54; N, 9.08.

Similarly, cis-4,5-dicarbomethoxy-1,6-diphenyl-3,3a-di(4-methoxyphenyl)-4,5-dihydropyrazolino[2,3-c][1,2,3]-triazole (10c), mp 233°, was obtained in a 60% yield in the reaction of 2c with dimethyl maleate.

Anal. Calcd for $C_{34}H_{32}N_4O_6$: C, 68.92; H, 5.41; N, 9.46. Found: C, 69.30; H, 4.96; N, 9.15.

Treatment of 1,2-bisphenylazocyclohexene (26) with dimethyl maleate gave a 51% yield of cis 4,5-dicarbomethoxy-1,6-diphenyl-3,3a-tetramethylene-4,5-dihydropyrazolino-[2,3-c][1,2,3] triazole (31), mp 182°.

Anal. Calcd for $C_{24}H_{26}N_4O_4$: C, 66.36; H, 5.99; N, 12.90. Found: C, 66.57; H, 6.15; N, 13.13.

The nmr and ir spectral data of these compounds have been summarised in Tables 3.2 and 3.4, respectively.

Reaction of 1,2-Bisphenylazostilbene (2a) with Maleic Anhydride

Treatment of 2a with maleic anhydride gave a 71% yield of 1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c][1,2,3]-triazole-4,5-dicarboxylicanhydride (11), mp 228°.

Anal. Calcd for $C_{30}H_{22}N_4O_3$: C, 74.08; H, 4.53; N, 11.53. Found: C, 74.12; H, 4.62; N, 11.35.

Reactions of 1,2-Bisphenylazoalkenes (2a-c and 26) with Dimethyl Fumarate

Treatment of 2a with dimethyl fumarate gave a 74% yield of trans-4,5-dicarbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c][1,2,3]triazole (12a), mp 205°.

Anal. Calcd for $C_{32}H_{28}N_4O_4$: C, 72.15; H, 5.26; N, 10.53. Found: C, 71.91; H, 5.33; N, 10.61.

Treatment of 2b with dimethyl fumarate gave the corresponding cycloadduct 12b, mp 212° in a 54% yield.

Anal. Calcd for $C_{32}H_{26}N_4O_4Cl_2$: C, 64.00; H, 4.33; N, 9.33. Found: C, 63.82; H, 4.42; N, 9.45.

Similarly, the reaction of 2c with dimethyl fumarate gave a 66% yield of trans 4,5-dicarbomethoxy-1,6-diphenyl-3,3a-di(4-methoxyphenyl)-4,5-dihydropyrazolino[2,3-c][1,2,3]-triazole (12c), mp 235°.

Anal. Calcd for $C_{34}H_{32}N_4O_6$: C, 68.92; H, 5.41; N, 9.46. Found: C, 68.58; H, 4.96; N, 9.15.

Treatment of bisphenylazocyclohexene (26) with dimethyl fumarate gave a 39% yield of trans-4,5-dicarbomethoxy-1,6-diphenyl 3,3a-tetramethylene-4,5-dihydropyrazolino[2,3-c][1,2,3]triazole (30), mp 180°.

Anal. Calcd for $C_{24}H_{26}N_4O_4$: C, 66.36; H, 5.99; N, 12.90. Found: C, 66.05; H, 5.88; N, 13.20.

Reaction of 1,2-Bisphenylazostilbene (2a) with Methyl Crotonate

Treatment of 2a with methyl crotonate gave a 45% yield of 1,3,3a,6-tetraphenyl-4-carbomethoxy-5-methyl-4,5-dihydro-pyrazolino[2,3-c][1,2,3] triazole (13), mp 203°.

Anal. Calcd for $C_{31}H_{28}N_4O_2$: C, 77.32; H, 5.52; 10.05. Found: C, 77.54, H, 5.54; 9.99.

Reaction of 1,2-Bisphenylazostilbene (2a) with trans-Dibenzoyl ethylene

Reaction of 2a with trans-dibenzoyl ethylene gave a 31% yield of trans-4,5-dibenzoyl-1,3,3a,6-tetraphenyl-4,5-dihydro-pyrazolino[2,3-c][1,2,3] triazole (14), mp 190°.

Anal. Calcd for $C_{42}H_{32}N_4O_2$: C, 80.99; H, 4.83; N, 8.99. Found: C, 81.01; H, 4.79; N, 8.87.

The nmr, uv and ir spectral data of these adducts are summarised in Tables 3.3, 3.4 and 3.5, respectively.

Reaction of 1,2-Bisphenylazoalkenes (2a-c and 26) with Ethyl Acrylate

Treatment of 1,2-bisphenylazostilbene (2a) with ethyl acrylate gave a 79% yield of 1,3,3a,6-tetraphenyl-4-carboethoxy-4,5-dihydropyrazolino[2,3-c][1,2,3] triazole (15a), mp 216°.

Anal. Calcd for $C_{31}H_{28}N_4O_2$: C, 76.23; H, 5.73; N, 11.47. Found: C, 76.47; H, 5.49; N, 11.76.

Similarly, the reaction of 2b with ethyl acrylate gave a 70% yield of the corresponding cycloadduct (15b), mp 164°.

Anal. Calcd for $C_{31}H_{26}N_4O_2Cl_2$: C, 66.91; H, 4.68; N, 10.07. Found: C, 66.56; H, 4.48; N, 10.51.

The reaction of 2c with ethyl acrylate gave a 74% yield of 15c, mp 158°.

Anal. Calcd for $C_{33}H_{32}N_4O_2$: C, 72.26; H, 5.84; N, 10.22. Found: C, 71.84; H, 5.97; N, 9.81.

On the other hand, the reaction of 1,2-bisphenyl-azocyclohexene (26) with ethyl acrylate gave a 61% yield of the corresponding dihydropyrazolotriazole derivative 33, mp 194°.

Anal. Calcd for $C_{23}H_{26}N_4O_2$: C, 70.77; H, 6.67; N, 14.36. Found: C, 71.02; H, 6.58; N, 14.49.

The nmr, uv and ir data of these adducts are summarised in Tables 3.3, 3.4 and 3.5, respectively.

Reaction of 1,2-Bisphenylazoalkenes (2a-c and 26) with Acrylonitrile

Treatment of 1,2-bisphenylazostilbene (2a) with acrylonitrile gave a 82% yield of 1,3,3a,6-tetraphenyl-4-cyano-4,5-dihydropyrazolino[2,3-c][1,2,3] triazole (16a), mp 249°.

Anal. Calcd for $C_{29}H_{23}N_5$: C, 78.91; H, 5.21; N, 15.80.
Found: C, 78.91; H, 5.30; N, 15.68.

Similarly, the reaction of 2b with acrylonitrile gave 16b, mp 242° , in 74% yield.

Anal. Calcd for $C_{29}H_{21}N_5Cl_2$: C, 68.37; H, 4.13;
N, 13.75. Found: C, 68.17; H, 3.92; N, 14.02.

On the other hand, the reaction of 2c with acrylonitrile gave the corresponding dihydropyrazolotriazole (16c), mp 206° , in 62% yield.

Anal. Calcd for $C_{31}H_{27}N_5O_2$: C, 74.25; H, 5.39;
N, 13.97. Found: C, 74.40; H, 5.29; N, 13.71.

The reaction of acrylonitrile with 1,2-bisphenylazocyclohexene (26) gave a 55% yield of 1,6-diphenyl-3,3a-tetramethylene-4-cyano-4,5-dihydropyrazolino[2,3-c] [1,2,3]-triazole (34), mp 203° .

Anal. Calcd for $C_{21}H_{21}N_5$: C, 73.47; H, 6.12; N, 20.41.
Found: C, 72.99; H, 5.99; N, 20.55

Reaction of 1,2-Bisphenylazostilbene (2a) with Methyl Methacrylate

Treatment of 2a with methyl methacrylate gave a 54% yield of 1,3,3a,6-tetraphenyl-4-methyl-4-carbomethoxy-4,5-dihydropyrazolino[2,3-c] [1,2,3] triazole (17), mp 249° .

Anal. Calcd. for $C_{31}H_{28}N_4O_2$: C, 77.32; H, 5.52; N, 10.05. Found: C, 77.42; H, 5.51; N, 10.10.

The nmr, uv and ir spectral characteristics of all these adducts have been tabulated in Tables 3.3, 3.4 and 3.5, respectively.

Reaction of 1,2-Bisphenylazoalkenes (2a-c and 26) with Phenyl Isocyanate

In a representative run, 1 mmol of the bisphenylazoalkene and 1 mmol of phenyl isocyanate in 2 ml acetone was refluxed for 1 hr. The solvent was removed under reduced pressure and the residue was recrystallised from a mixture (3:1) of benzene and ethyl acetate to give the corresponding 1,2,4-triazolidino [1,5-c] [1,2,3] triazol-5-one. Table 3.10 summarises the analytical results. The ir spectral data of various triazolidinotriazolones are given in Table 3.5.

Reaction of 1,2-Bisphenylazoalkenes (2a-c and 26) with Phenyl Isothiocyanate

In a typical run 1 mmol of the bisphenylazoalkene and 1 mmol of phenyl isothiocyanate in 2 ml acetone was refluxed for 2 hr. Removal of acetone, followed by recrystallisation of the residue from a mixture (2:1) of benzene and ethyl acetate yielded the corresponding 1,2,4-triazolidino [1,5-c] [1,2,3] triazol-5-thiones. Table 3.8 summarises

Table 3.8

Cycloaddition of 1,2-Bisphenylazoalkenes (2a-c and 26) to Phenyl Isocyanate and Phenyl Isothiocyanate

Bisphenylazoalkene	Dipolarophile	Cycloadduct	Yield %	Mp °C	Molecular Formula	Analysis					
						Calcd (%)			Found (%)		
						C	H	N	C	H	N
<u>2a</u>	C_6H_5NCO	<u>18a</u>	48	238	$C_{33}H_{25}N_5O$	78.11	4.93	13.8	78.22	5.00	13.6
	C_6H_5NCS	<u>19a</u>	60	268	$C_{33}H_{25}N_5S$	75.71	4.78	13.39	75.76	5.1	13.3
<u>2b</u>	C_6H_5NCO	<u>18b</u>	62	226	$C_{33}H_{23}N_5OCl_2$	68.87	4.00	12.17	69.05	4.21	11.95
	C_6H_5NCS	<u>19b</u>	54	244	$C_{33}H_{23}N_5SCl_2$	67.00	3.89	11.84	67.39	3.66	12.05
<u>2c</u>	C_6H_5NCO	<u>19a</u>	56	217	$C_{35}H_{29}N_5O_3$	74.07	5.11	12.35	73.67	5.33	11.95
	C_6H_5NCS	<u>19b</u>	50	231	$C_{35}H_{29}N_5O_2S$	74.04	4.97	12.00	72.35	4.85	12.23
<u>26</u>	C_6H_5NCO	<u>35</u>	45	209	$C_{25}H_{23}N_5O$	73.35	5.62	17.11	73.08	5.78	16.95
	C_6H_5NCS	<u>36</u>	42	217	$C_{25}H_{23}N_5S$	70.59	5.41	16.41	70.32	5.62	16.71

the percentage yields, analytical results. The ir spectral data of these adducts are summarised in Table 3.5.

Reaction of 2,3-Bisphenylazo-2-butene (20) with Carbon Disulphide in Presence of Dry Hydrogen Chloride

Into a mixture of 0.52 g (2 mmol) of 2,3-bisphenylazo-2-butene and dry carbon disulphide (3 ml) in dry benzene (10 ml) was passed a stream of dry HCl for 5 minutes during which the intense colour of the solution disappeared. The unchanged carbon disulphide and the solvent was removed under reduced pressure. The residue was treated with a mixture (1:1) of benzene and petroleum ether (bp 60-80°) (10 ml), to extract out the organic fractions. The residue (50 mg, 76%) was identified as elemental sulphur. The solvent was removed from the benzene-petroleum ether (bp 60-80°) extract and the residue was digested with dilute hydrochloric acid for 15 minutes, to remove the phenyl isothiocyanate formed as one of the products. Extraction with ether gave a product which was distilled under reduced pressure to give 0.21 g (60%) of 2-phenyl-4,5-dimethyl-1,2,3-triazole, mp 35°, (bp 162° at 60 mm) which was identified by comparing its ir spectrum with that of an authentic sample.¹⁸

Reaction of 2,3-Bisphenylazo-2-butene (20) with Dimethyl Acetylenedicarboxylate in Presence of Dry Hydrogen Chloride

Dry hydrogen chloride was passed into a solution of

0.26 g (1 mmol) of 2,3-bisphenylazo-2-butene (20) and 0.14 g (1 mmol) of dimethyl acetylenedicarboxylate in 10 ml of dry benzene for 5 minutes, when the intense colour of the solution had fully disappeared. The solution was washed free of hydrochloric acid with water, and removal of the solvent from the organic layer gave a product which was recrystallised from a mixture (1:1) of petroleum ether (bp 60-80°) and benzene to give 0.25 g (62%) of 2,6-diphenyl-3,3a-dimethyl-4,5-dicarbomethoxypyrazolino[2,3-c][1,2,3] triazole (25), mp 136°.

Anal. Calcd for $C_{22}H_{22}N_4O_4$: C, 65.08; H, 5.42; N, 13.79. Found: C, 65.11; H, 5.45; N, 13.74.

The ir spectrum (KBr) of 25 showed peaks at 1745 and 1690 cm^{-1} (C=O), 1575, 1565, 1490, 1460, 1405, 1370, 1345, 1322, 1250, 1215, 1170, 1095, 1050, 980, 760, 740, 695 and 677 cm^{-1} .

The nmr spectrum (CDCl_3) of 25 showed peaks at 1.55 δ (3 H, s) and 1.90 δ (3 H, s) due to CH_3 protons, 3.75 δ (3 H, s) and 3.85 δ (3 H, s) due to carbomethoxy protons and at 7.50 δ (10 H, m) due to phenyl protons.

Thermolysis of cis-4,5-Dicarbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c][1,2,3] triazole (10a)

Heating 200 mg (0.5 mmol) of the dihydropyrazolino-triazole 10a at 200° for 30 minutes and subsequent chromatographic work-up of the reaction product gave 105 mg (87%) of

2,4,5-triphenyl-1,2,3-triazole (5a), mp 124° (mmp)³.

Thermolysis of trans-4,5-Dicarbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino [2,3-c] [1,2,3] triazole (12a)

Thermolysis of 200 mg (0.5 mmol) of 12a as in the previous case gave 93 mg (80%) of 5a, mp 124° (mmp)³.

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CHAPTER 4

VALENCE ISOMERISM IN ENEDIIMINES, 2,3-DIHYDROPYRAZINES AND THE DIANILS OF 1,4-DICARBONYLALKENES

4.1 ABSTRACT

The enediimine obtained in the reaction of o-phenylenediamine and benzaldehyde has been shown to undergo valence isomerisation to 1-benzyl-2-phenylbenzotriazole. The intermediate, benzimidazolium ylide could not be trapped by treatment with dipolarophiles. The enediimines derived from 5,6-diphenyl-2,3-dihydropyrazine as well as 2,3,5,6-tetraphenyl-2,3-dihydropyrazine also rearranged to the corresponding imidazoles through their valence isomeric intermediates. The

azomethine ylides in these cases also could not be trapped through cycloaddition reactions. The unexpected inertness of these systems towards dipolarophiles has been explained in terms of their facile rearrangement to the corresponding imidazoles, in preference to cycloaddition reactions. The reaction of o-phthalaldehyde with aniline in presence of different dipolarophiles gave in each case 1-phenylimino-2-phenylisindoline and not the expected cycloadducts.

4.2 RESULTS AND DISCUSSION

In Chapter 2 of this thesis we have shown that 1,2-bis-phenylazoalkenes exist in valence tautomeric equilibrium with anhydro 1-phenylimino-2-phenyl-4,5-disubstituted-1,2,3-triazolium hydroxides and that they undergo thermal and photochemical fragmentation to give 1,2,3-triazoles. In Chapter 3, we have shown that the 1,3-dipolar cycloaddition reactions of such anhydro iminotriazolium derivatives to acetylenic and olefinic dipolarophiles can be advantageously used in the synthesis of condensed heterocyclic ring systems.

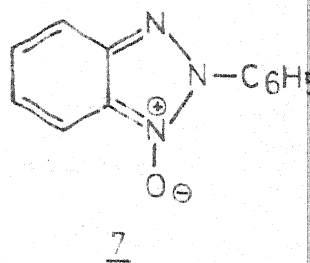
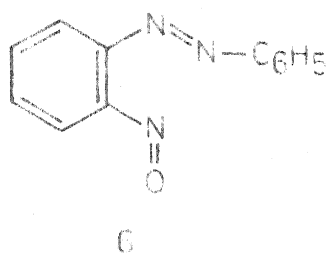
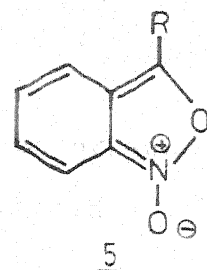
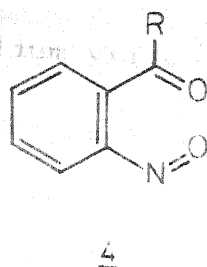
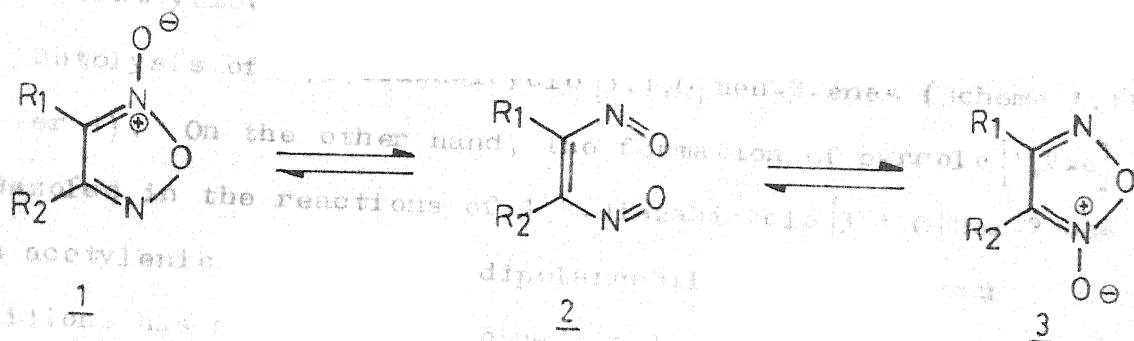
The 1,2-bisphenylazoalkenes can be considered as representative examples of a hetero-1,3,5-hexatrienoid system. The existence of valence isomerism in these systems prompted us to investigate whether such a behaviour is general in other heterohexatrienoids as well. In this connection, it may be pointed out that valence isomeric structures have been

invoked to explain some of the transformations of 1,2-dinitrosoalkenes as well as β -nitroso- α,β -unsaturated carbonyl compounds. The controversy regarding the structure of furoxan derivatives has been discussed in detail in Chapter 1 (section 1.5.2). In order to explain the rapid interconversion in assymmetrically substituted furoxans, different workers have proposed a dynamic equilibrium between furoxans and their valence isomeric, 1,2-dinitrosoalkenes.^{1,2,3}

The results of Gibson⁴, Gladstone and coworkers⁵ and Chattaway and Parker⁶ have shown that aromatic compounds containing a carbonyl and a nitroso functions, ortho with respect to each other exist in their valence isomeric, anthranil-1-oxide form (Scheme 4.1). Recent investigations by Huisgen and Weberndorfer⁶ and Grashey⁷ have demonstrated the existence of valence isomerism in o-nitrosoazobenzenes, and also the ready transformation of these derivatives to the isomeric benzotriazole 1-oxides (Scheme 4.1).^{7,8}

The recent investigations by Padwa, Schmid and others have proved that 2,3-dihydropyridazines under appropriate conditions exist in all the four possible valence isomeric forms, namely, the 2,3-dihydropyrazine form, the open-chain enediimine form, the 1,3-diazabicyclo[3,1,0]hex-3-ene form and the dipolar imidazolium ylide form.⁹⁻¹⁴ Thus, Padwa and coworkers¹¹ have demonstrated that 1,3-diazabicyclo[3,1,0]hex-3-enes under photochemical conditions undergo ring opening

Scheme 4.1



to enediimines which subsequently cyclise to 2,3-dihydropyrazines. These authors have invoked the intermediacy of dipolar imidazolium ylides to explain the formation of imidazoles during the photolysis of 1,3-diazabicyclo[3,1,0]hept-3-enes (Scheme 1.11, Chapter 1). On the other hand, the formation of pyrrolo[1,2-c]-imidazoles in the reactions of 1,3-diazabicyclo[3,1,0]hept-3-ene with acetylenic and olefinic dipolarophiles under thermal conditions has also been explained in terms of intermediate dipolar imidazolium ylides.¹⁵ Beak and Miesel¹⁶ have shown that 2,3-dihydropyrazines also are converted photochemically to the corresponding imidazoles through the intermediacy of imidazolium ylides¹⁶ (Scheme 1.12, Chapter 1).

Our results regarding the chemistry of 1,2-bisphenylazoalkenes suggested that conditional to there being a cisoid geometry in the heterohexatrienoids, the valence isomerisations in these systems should be facile under thermal conditions. In order to verify this, we have attempted the synthesis of some pyrrolo[1,2-c]imidazoles or their derivatives, starting from enediimines as well as 2,3-dihydropyrazines.

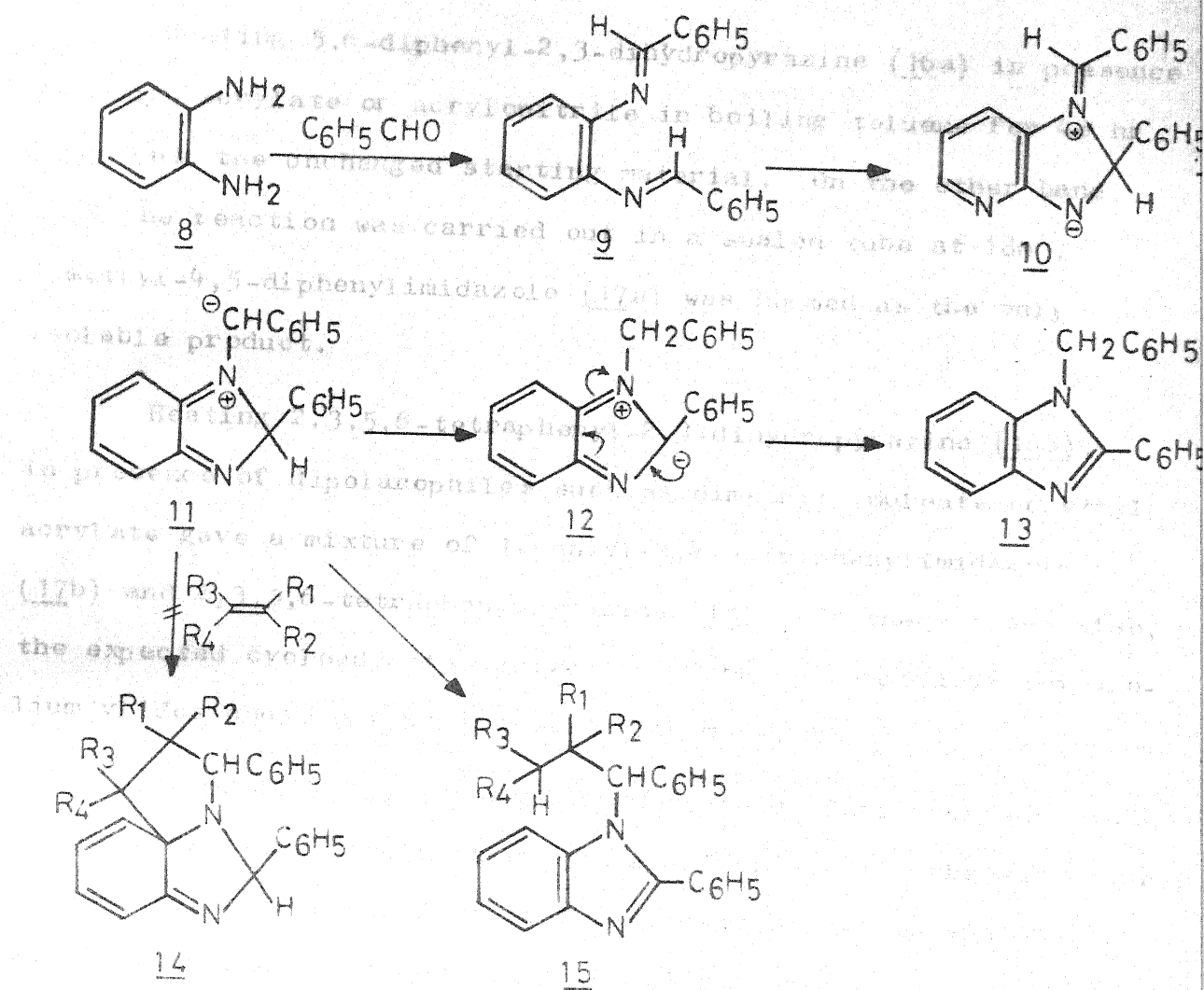
As early as 1889, Fischer had reported the formation of 1-benzyl-2-phenylbenzimidazole in the reaction of benzaldehyde with *o*-phenylenediamine.^{17,18} Though, *N,N'*-dibenzal-*o*-phenylenediamine has been recognised as the intermediate in this reaction, it has not so far been isolated because of its subsequent transformation. It is reasonable to assume that valence

isomeric structures such as 10 and 11 are involved in the conversion of N,N'-dibenzal-o-phenylenediamine to 1-benzyl-2-phenylbenzimidazole (Scheme 4.2). We felt that it should be possible to trap an intermediate like 11 through a 1,3-dipolar cycloaddition reaction to give cycloadducts such as 14 or a simple nucleophilic addition product like 15 (Scheme 4.2).

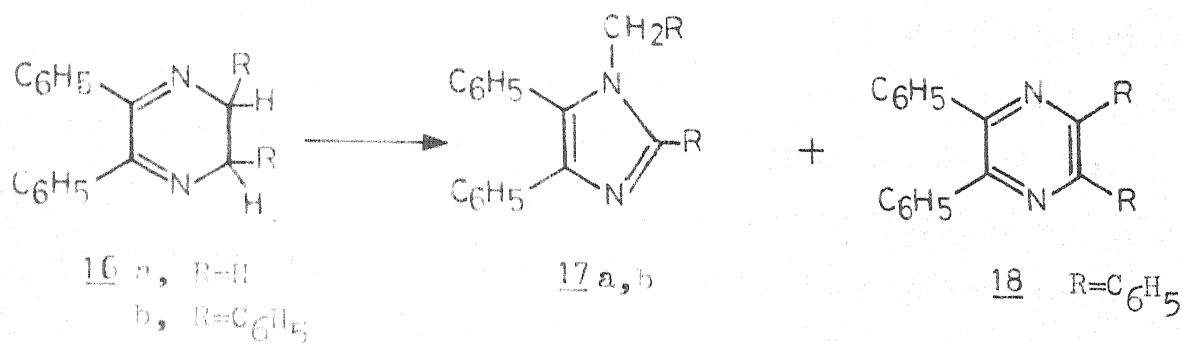
N,N'-Dibenzal-o-phenylenediamine (9) was prepared by mixing previously cooled (-20°) methanolic solutions o-phenylenediamine and benzaldehyde in a 1:4 molar ratio. The solid enediimine derivative (9) was then suspended in cold etherial solutions of dipolarophiles such as dimethyl maleate, dimethyl fumarate, ethyl acrylate and acrylonitrile. On allowing to warm up, in each case only 1-benzyl-2-phenylbenzimidazole could be isolated. Failure to isolate products like 14 or 15 suggests a very facile transformation of the intermediate 11 to 13. The loss of aromatic stabilisation in the formation of products like 14 could also be a factor in favour of products like 13.

In continuation of our studies, we have attempted at generating enediimines through a thermal electrocyclic ring opening of an appropriate 2,3-dihydropyrazine derivative. Our aim was to trap the enediimines in their valence isomeric imidazolium ylide form. With this view, we have prepared two dihydropyrazine derivatives, namely, 5,6-diphenyl-2,3-dihydropyrazine (16a) and 2,3,5,6-tetraphenyl-2,3-dihydropyrazine (16b) by the reaction of the corresponding ethylenediamine with benzil.

Scheme 4.2



Scheme 4.3

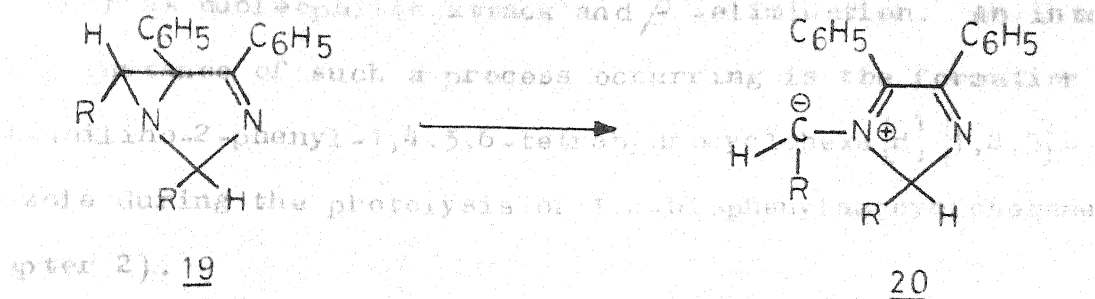


Heating 5,6-diphenyl-2,3-dihydropyrazine (16a) in presence of ethyl acrylate or acrylonitrile in boiling toluene for 48 hr gave back the unchanged starting material. On the other hand, when the reaction was carried out in a sealed tube at 180°, 1-methyl-4,5-diphenylimidazole (17a) was formed as the only isolable product.

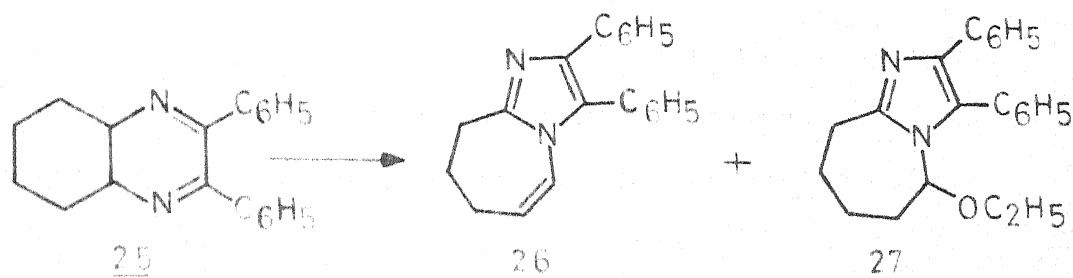
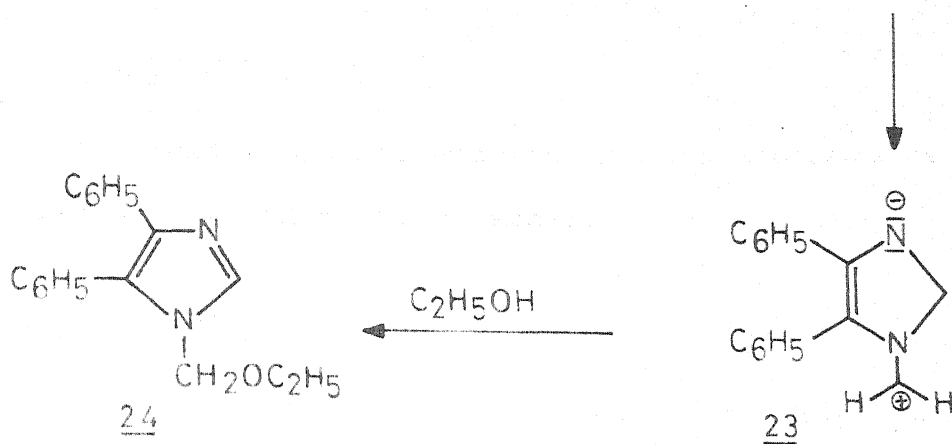
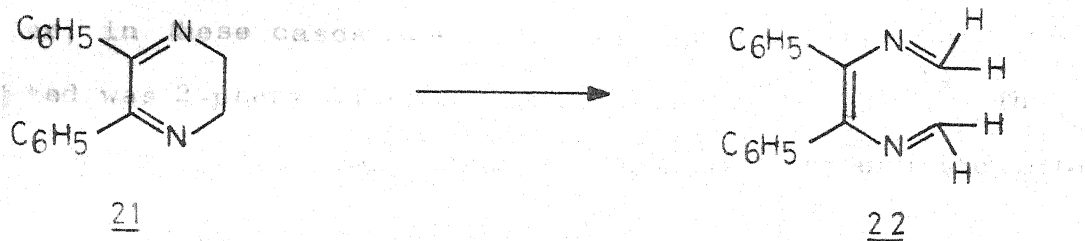
Heating 2,3,5,6-tetraphenyl-2,3-dihydropyrazine (16b), in presence of dipolarophiles such as dimethyl maleate or ethyl acrylate gave a mixture of 1-benzyl-2,4,5-triphenylimidazole (17b) and 2,3,5,6-tetraphenylpyrazine (18). In these cases also, the expected cycloadducts derived from the corresponding imidazolium ylides could not be isolated (Scheme 4.3).

One probable reason for the failure to form cycloadducts in these reactions could be due to a difference in the structure of the dipolar species derived from dihydropyrazines via the enediimines and those derived from 1,3-diazabicyclo[3,1,0]hex-3-enes (Scheme 4.4). It is probable that in the former case, the azomethine ylide is formed such that the positive end of the dipole is exocyclic (23) whereas in the latter, it is predominantly within the ring (20). The formation of products such as 24, 26 and 27 as reported by Beak and Miesel¹⁶ during the photolysis of dihydropyrazines 21 and 25 would also support this view. However, it may be premature to make any such generalization without additional experimental evidences. It may be pointed out that at least under photochemical conditions, the positive end of the

Scheme 4.4



In continuation of our studies we have investigated reaction between phthalazine derivatives and electrophilic aromatic species such as dimethyl sulfoxide.



1,3-dipole could participate in reactions typical of carbonium ions such as nucleophilic attack and β -elimination. An interesting instance of such a process occurring is the formation of 1-anilino-2-phenyl-1,4,5,6-tetrahydrocyclohexa [d] [1,2,3]-triazole during the photolysis of 1,2-bisphenylazocyclohexene (Chapter 2).

In continuation of our studies, we have investigated the reaction between phthalaldehyde and aniline in presence of dipolarophiles such as dimethyl maleate and ethyl acrylate. However, in these cases also, the only product that could be isolated was 2-phenyl-1-phenyliminoisoindoline (33).¹⁹ The formation of 33, however, could be explained through the intermediates like 30 and 32 (Scheme 4.5).

4.3 EXPERIMENTAL

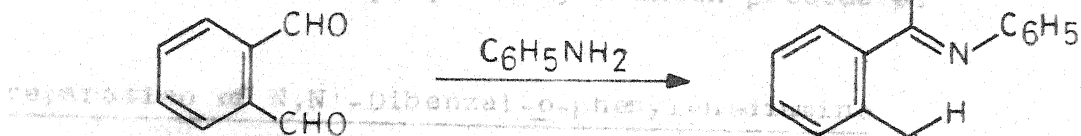
All melting points are uncorrected and have been recorded on Meltemp, melting point apparatus.

Starting Materials

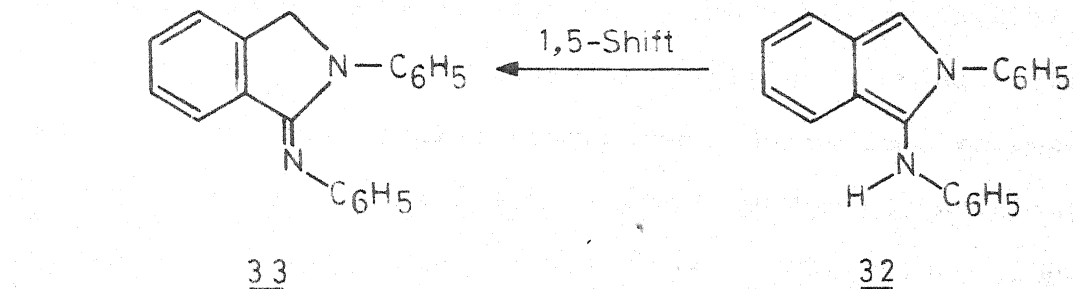
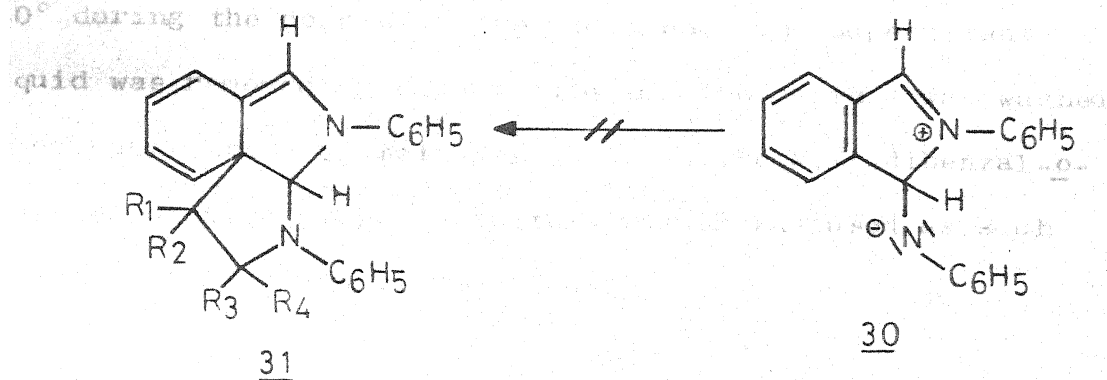
Aniline, benzaldehyde, *o*-phenylenediamine, *o*-phthalaldehyde, dimethyl maleate and ethyl acrylate were purified by distillation or recrystallisation, before use. 4,5-Diphenyl-4,5-dihydropyrazine, mp 162°, (16a) was prepared by the reaction between benzil and ethylenediamine as per a reported procedure.²⁰ 2,3,5,6-Tetraphenyl-2,3-dihydropyrazine, mp 192°, (16b) was

Scheme 4.5

...in a similar manner by the reaction of benzil and 1,2-diphenylethylenediamine. 1,2-Diphenylethylenediamine, itself was prepared by a known procedure.



A solution of 10 g (0.1 mole) of p-phenylenediamine in 50 ml methanol, cooled to 20° was added to a solution of 29 in 100 ml methanol, cooled to 20°. The mixture was stirred for 2 hours and then poured into 120 ml of methanol. The solid was filtered and dried at 0° during the night. The solid was a white powder.



prepared in a similar manner by the reaction of benzil and 1,2-diphenylethylenediamine. 1,2-Diphenylethylenediamine, mp 122° , itself was prepared by a known procedure.²¹

Preparation of N,N'-Dibenzal-o-phenylenediamine

A solution of 10 g (0.1 mole) of o-phenylenediamine in 50 ml methanol, cooled to -20° was added slowly with stirring to a solution of 40 g (0.4 mole) of benzaldehyde in 120 ml of methanol, and the mixture was maintained around -20° during the course of the addition. The supernatant liquid was removed by decantation and the residue was washed repeatedly with cold methanol (-20°). The N,N'-dibenzal-o-phenylenediamine prepared in this manner was used as such immediately for further reactions.

Reaction between N,N'-Dibenzal-o-phenylenediamine and Dimethyl Maleate

A suspension of 1 g (5 mmol) N,N'-dibenzal-o-phenylene-diamine in a solution of 4 g (25 mmol) dimethyl maleate in 75 ml ether was stirred at -20° for 3 hr. The solution was allowed to warm up to room temperature, under stirring. The solvent was removed by distillation and the residue on recrystallization from ethanol gave 0.92 g (92%) of 1-benzyl-2-phenylbenzimidazole, (13), mp 296° (lit.¹⁸ mp). The mother liquor on distillation gave the unreacted dimethyl maleate.

Reaction between N,N'-Dibenzal-o-phenylenediamine and Ethyl Acrylate

Treatment of N,N'-dibenzal-o-phenylenediamine (1 g, 5 mmol) and ethyl acrylate (10 g, 110 mmol) as in the earlier case gave 0.9 g (90%) of 1-benzyl-2-phenylbenzimidazole, mp 296° (mmp).

Thermolysis of 4,5-Diphenyl-2,3-dihydropyrazine in Presence Dimethyl Maleate

A solution of 0.3 g (1 mmol) of 4,5-diphenyl-2,3-dihydropyrazine and 0.56 g (4 mmol) dimethyl maleate in 3 ml of toluene was heated in a sealed tube at 180° for 12 hr. The reaction mixture was then chromatographed over a column of alumina. Elution with petroleum ether (bp 60-80) gave 0.5 g of unchanged dimethyl maleate. Continued elution with benzene containing 5% ethyl acetate gave 0.21 g (70%) of 1-methyl-4,5-diphenylimidazole, (17a), mp 158° (lit.²² mp 159°).

Reaction of 4,5-Diphenyl-2,3-dihydropyrazine in Presence of Ethyl Acrylate

Heating 0.3 g (1 mmol) of 4,5-diphenyl-2,3-dihydropyrazine and 0.9 g (10 mmol) ethyl acrylate as in the earlier case gave 0.2 g (66%) of 1-methyl-4,5-diphenylimidazole (17a), mp 158°, (mmp).

Thermolysis of 2,3,5,6-Tetraphenyl-2,3-dihydropyrazine (16b)
in Presence of Dimethyl Maleate

A solution of 0.25 g (0.5 mmol) 2,3,5,6-tetraphenylpyrazine and 0.6 g (4 mmol) of dimethyl maleate in 3 ml toluene was refluxed for 6 hr. Removal of toluene by distillation and treatment of the residue with ethanol gave 0.17 g (72%) of tetraphenylpyrazine, (18), mp 249° (lit.²³ mp 249-250°) as an insoluble residue. Concentration of the mother liquor provided 15 mg (6%) of 1-benzyl-2,4,5-triphenylimidazole, (17b), mp 168° (lit.²⁴ mp 168-69°).

Thermolysis of 2,3,5,6-Tetraphenyl-2,3-dihydropyrazine (16b)
in Presence of Ethyl Acrylate

Heating 0.25 g (0.5 mmol) of (16b) and .9 g (10 mmol) ethyl acrylate as in the earlier case gave 0.19 g (77%) of 18, mp 249° (mmp) and 12 mg (5%) of 17b, mp 168° (mmp).

Reaction Between o-Phthalaldehyde and Aniline in Presence
of Ethyl Acrylate

Into a solution of 3 g (.025 mol) of aniline in 10 ml of benzene was added, under stirring, a mixture of 1 g (.01 mol) of phthaldehyde and 9 g (.1 mol) ethyl acrylate. The stirring was continued for 2 hr. Removal of the solvent and recrystallization of the residue from benzene gave 2.1 g (70%) of 1-phenylimino-2-phenylisoindoline, (33), mp 142° (lit.¹⁹ mp 142-143°).

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VITAE

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